



Source-Flux-Fate Modelling of Priority Pollutants in Stormwater Systems

Vezzaro, Luca

Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Vezzaro, L. (2011). *Source-Flux-Fate Modelling of Priority Pollutants in Stormwater Systems*. Technical University of Denmark.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Source-Flux-Fate Modelling of Priority Pollutants in Stormwater Systems



Luca Vezzaro

Source-Flux-Fate Modelling of Priority Pollutants in Stormwater Systems

Luca Vezzaro

PhD Thesis
March 2011

DTU Environment
Department of Environmental Engineering
Technical University of Denmark

Luca Vezzaro

Source-Flux-Fate Modelling of Priority Pollutants in Stormwater Systems

PhD Thesis, March 2011

The thesis will be available as a pdf-file for downloading from the homepage of the department: www.env.dtu.dk

Address: DTU Environment
Department of Environmental Engineering
Technical University of Denmark
Miljoevej, building 113
DK-2800 Kgs. Lyngby
Denmark

Phone reception: +45 4525 1600
Phone library: +45 4525 1610
Fax: +45 4593 2850

Homepage: <http://www.env.dtu.dk>
E-mail: reception@env.dtu.dk

Printed by: Vester Kopi
Virum, March 2011

Cover: Torben Dolin

ISBN: 978-87-92654-26-7

Preface

This thesis is based on the scientific results obtained during the PhD project at the Department of Environmental Engineering (DTU Environment), Technical University of Denmark (DTU) in the period from January 2007 to December 2010. The project was conducted under the supervision of Associate Professor Peter Steen Mikkelsen and Professor Anna Ledin. The PhD project was funded by DTU and part of the results were obtained with supplementary financial support from the EU funded project ScorePP (Source Control Options for Reducing Emission of Priority Pollutants).

The content of the thesis is based on the results presented in five scientific papers, which have been published or submitted to peer reviewed journals or conferences. These articles are referred in the text with the associated Roman number (e.g. **Paper IV**).

- I. **Vezzaro, L.**, Mikkelsen, P.S.; Application of global sensitivity analysis and uncertainty quantification in dynamic modelling of micropollutants in stormwater runoff. Submitted manuscript.
- II. **Vezzaro, L.**, Eriksson, E., Ledin, A., Mikkelsen, P.S. (2010); Dynamic stormwater treatment unit model for micropollutants (STUMP) based on substance inherent properties. *Water Science and Technology*; **62**(3), 622-629.
- III. **Vezzaro, L.**, Eriksson, E., Ledin, A., Mikkelsen, P.S.; Modelling the fate of organic micropollutants in stormwater ponds. Submitted manuscript.
- IV. **Vezzaro, L.**, Eriksson, E., Ledin, A., Mikkelsen, P.S.; Quantification of uncertainty in modelled partitioning and removal of heavy metals (Cu, Zn) in a stormwater retention pond and a biofilter; Submitted manuscript.
- V. **Vezzaro, L.**, Ledin, A., Mikkelsen, P.S. (2010). Integrated modelling of priority pollutants in stormwater systems. In: *Proceedings of IDRA 2010. XXXII Italian Conference of Hydraulics and Hydraulic Constructions*, Palermo, Italy, 14th-17th September 2010.

The papers above are not included in this www-version but can be obtained from the library at DTU Environment. Contact info: Library, Department of Environmental Engineering, Technical University of Denmark, Miljøvej, Building 113, DK-2800 Kgs. Lyngby, Denmark or library@env.dtu.dk.

The thesis also presents results that have not been published yet (especially in Section 4 and in Appendix VI and VII). The following articles and reports were prepared during the PhD project but they are not included as part of the thesis:

- Dotto, C.B.S., Mannina, Kleidorfer, M., **Vezzaro, L.**, Henrichs, M., McCarthy, D. T., Freni, G., Rauch, W., Deletic, A.; Comparison of different uncertainty techniques in urban stormwater quantity and quality modelling. Manuscript in preparation.
- Benedetti, L., **Vezzaro, L.**, Gevaert, V., De Keyser, W., Verdonck, F., De Baets, F., Nopens, I., Vanrolleghem, P.A., Mikkelsen, P.S. (2009). Dynamic Transport and Fate Models for Micro-Pollutants in Integrated Urban Wastewater Systems. In: *Proc. WEFTEC 09, 82nd Annual Water Environment Federation Technical Exhibition and Conference*, Orlando, Florida, USA, October 10-14, 2009
- **Vezzaro, L.**, Gevaert, V., Benedetti, L., De Keyser, W., Verdonck, F., Vanrolleghem, P.A., Boisson, P., Mikkelsen, P.S. (2009). Unit process models for fate of Priority Pollutants. ScorePP project deliverable D7.2.
- Benedetti, L., De Keyser, W., **Vezzaro, L.**, Atanasova, N., Gevaert, V., Verdonck, F., Vanrolleghem, P.A., Mikkelsen, P.S. (2009). Integrated dynamic urban scale sources-and-flux model for PPs. ScorePP project deliverable D7.4 (available at www.scorepp.eu).
- **Vezzaro, L.**, Cerk, M., Viavattene, C., Donner, E., Scholes, L., Ledin, A., Mikkelsen, P.S. (2009). Visualization elements, tools and demonstrations. ScorePP project deliverable D6.3 (available at www.scorepp.eu).
- **Vezzaro, L.** (2008). Sensitivity analysis and uncertainty evaluation of a conceptual stormwater quality model. In *Proceedings of the 11th International Conference on Urban Drainage*, Edinburgh, Scotland, UK, 31st August–5th September 2008.

Acknowledgments

This thesis is the result of almost four years of discussions and suggestions from my supervisors, Associate Professor Peter Steen Mikkelsen and Professor Anna Ledin. They were a great source of inspiration and they helped to direct my efforts (and simulations) in a meaningful direction.

Also, I would like to thank my colleagues at DTU Environment: Associate Professor Eva Eriksson, Associate Professor Hans-Christian Holten Lützhøft, Dr. Anitha Sharma, and Heidi Birch for supporting me with chemical expertise and for providing data and measurements. Many of the results presented in this thesis are the outcome of discussions with my past and present modelling colleagues Dr. Erik Lindblom (who also provided the starting point for this thesis), Anders Breinholt and Morten Borup. DMI rainfall data were accessed thanks to the collaboration of Associate Professor Karsten Arnbjerg-Nielsen.

This thesis deals with modelling, but any of the results presented here could not be achieved without the kind collaboration of several researchers and practitioners who provided the measurements used in the simulations. The stormwater quality data from Göteborg were kindly provided by Dr. Stefan Ahlman (formerly at Chalmers University, who also created the SEWSYS model, basis for the runoff quality model presented in the thesis), while access to rainfall measurements from Göteborg was provided by Claes Hernebring (DHI Sweden). The data regarding Lilla Essingen were provided by Eva Vall, Jens Fagerberg and Mathias von Scherling (Stockholm Vatten AB). The measurements from the retention pond in Oslo were provided by Svein Ole Åstebøl (COWI AS Oslo, Norway) and the Norwegian Road Administration, while Professor Jes Vollertsen (Aalborg University, Denmark) furnished me with information about the quality data. The biofilter data were supplied by Dr. Belinda Hatt (Monash University, Australia). The measurement campaign in Albertslund was partially financed by the Interreg IVB North Sea Region Programme via the project “Impact of Climate Change on the Quality of Urban and Coastal Waters (Diffuse Pollution) – DiPOL” and it was carried out in the collaboration of Hans-Henrik Høg (Albertslund municipality), Thomas Aabling and Søren Gabriel (Orbicon A/S).

Some of the approaches presented in the thesis were developed under the framework of the EU project “Source Control Options for Reducing Emission of Priority Pollutants - ScorePP” (contract no. 037036, a project coordinated by Department of Environmental Engineering, Technical University of Denmark (DTU) within the Energy, Environment and Sustainable Development section of the European Community’s Sixth Framework Programme for Research, Technological Development and Demonstration). Thus I would like to thank my colleagues spread across Europe (and Canada). Dr. Lorenzo Benedetti, Webbey De Keyser, Veerle Gevaert and Dr. Frederick Verdonck (Ghent

University, Belgium), Prof. Peter Vanrolleghem (Université Laval, Canada), and Pascal Boisson (Anjou Recherche, France) were involved in the development of urban fate models for Priority Pollutants (which include the STUMP model presented in this thesis). The use of GIS tools in stormwater pollution benefited from collaboration with Matej Cerk and Dr. Natasa Atanasova (University of Ljubljana, Slovenia); and with Dr. Lian Scholes, Dr. Erica Donner, and Dr. Christophe Viavattene (Middlesex University, United Kingdom).

The COST action 636 “Xenobiotics in the urban water cycle” financed a scientific mission to Chalmers University, Göteborg (Sweden), where I was hosted by Karin Bjorklund and Professor Per-Arne Malmqvist for interesting discussions about source characterization and modelling of dissolved micropollutants.

The use of uncertainty analysis and their application in stormwater quality models were the subject of discussion held among the participants in the International Working Group on Data and Models. The uncertainty analysis results presented in the thesis thus benefited from the collaboration with Assistant Professor Gabriele Freni (University Enna - Kore, Italy), Dr. Giorgio Mannina (University of Palermo, Italy), Dr Manfred Kleidorfer (University of Innsbruck, Austria), Cintia Dotto (Monash University, Australia) and Malte Henrichs (Muenster University of Applied Sciences, Germany). Finally, I would like to thank all my fellow PhD students at DTU Environment (and especially those of the UrbanWaterTech graduate school) for these four years. It was a pleasure to share all this time with you.

Jeg takker alle mine venner fra den 3. Vesterbro Vildgæssene spejdergruppe, fordi en spændende gruppe af venner er den bedste ting, som hjælper til at færdiggøre en ph.d. Thanks to all the friends who crossed my path in these years, and especially those who always had time for a coffee or a chat., Anna (grazie), Thomas (tak), Nana, (谢谢), Tutu (谢谢), Suzi (sağol), Maria (tak), Damiano (grazie), i membri della Bioti corporation (grazie, specialmente ad Elena), ed un grazie speciale ad Annamaria per tutto il tempo regalatomi. *Dulcis in fundo*, non posso fare di fare a meno di ringraziare le mie famiglie: quella che in questi anni di lontananza da Padova ha affrontato prove non certo facili; e i due fratelli acquisiti in questi cinque anni danesi, Chiara e Antonio, con i quali ho condiviso gli alti e bassi questa lunga avventura. Grazie.

Abstract

The increasing focus on management of stormwater Priority Pollutants (PP) enhances the role of mathematical models as support for the assessment of stormwater quality control strategies. This thesis investigates and presents modelling approaches that are suitable to simulate PP fluxes across stormwater systems, supporting the development of pollution control strategies. This is obtained by analyzing four study areas: (i) catchment characterization, (ii) pollutant release and transport models, (iii) stormwater treatment models, and (iv) combination of the above into an integrated model. Given the significant level of uncertainty affecting stormwater quality models, the identification of sources of uncertainty (based on Global Sensitivity Analysis - GSA) and quantification of model prediction bounds (based on pseudo-Bayesian methods, such as the Generalized Likelihood Uncertainty Estimation - GLUE) are presented as crucial elements in modelling of stormwater PP. Special focus is on assessing the use of combined informal likelihood measures assigning equal weights at different model outputs (flow and quality measurements).

Management of the spatially heterogeneous sources of stormwater PP requires a detailed catchment characterization, based on land use and the use of information stored in Geographical Information System (GIS). The analysis carried out in the thesis, which compares different characterization approaches with different level of detail, suggests in fact that this approach allows the identification of the major pollutant sources (and sources of uncertainty) in the catchment and provides the basis for the development of source-control strategies.

The thesis shows how conceptual continuous dynamic models, combined with uncertainty analysis, can provide estimation of PP loads that can be used for scenario analysis over long time periods. The combination of GSA with uncertainty analysis techniques enables the identification of interactions between model factors which are commonly ignored by traditional approaches. The analysis performed in the thesis shows how the use of different informal likelihood measures in GLUE can affect the estimation of model prediction bounds and the model applications for stormwater management.

The fate of stormwater PP (dissolved and particulate) in treatment units is simulated by extending a dynamic multi compartmental stormwater treatment model with fate processes that are simulated based on the substance inherent properties (degradation rates, solid-water partition coefficient, Henry's law

constant, molecular weight). The developed model (STUMP) thus applies concepts commonly used in chemical risk assessment at the scale of stormwater treatment facilities by providing a dynamic representation of the system. STUMP can simulate different substances (metals, organics) in various treatment units (e.g. ponds, biofilters). The uncertainty analysis performed in the thesis allows the identification of the major sources of uncertainty in different units, depending on the dominating PP fate processes. A reduction in STUMP uncertainty of PP fate estimation can be obtained by a good representation of the physical characteristic of the treatment unit, reducing the need for PP field measurements.

The thesis shows how the integration of the investigated models provides results that can be used in the development, assessment, and comparison of different PP control strategies (e.g. source control or improvement of treatment facilities). The combination of the integrated model with uncertainty analysis identifies the information that is necessary to improve the scenario analysis and increase the reliability of the simulation results. The models developed and demonstrated in the thesis are applied in a real catchment to evaluate different scenarios for reduction of PP emissions to the aquatic environment, showing the potential of the proposed approaches as support tools in stormwater quality management.

The thesis provides a framework for the trustworthy application of models to estimate PP fluxes from their sources, and through stormwater drainage systems, and to the sink. This fills a knowledge gap regarding stormwater PP and it supplies urban water managers with modelling tools for management of stormwater pollution. Examples in the thesis are focused on heavy metals (Cu, Zn) and selected organic substances (DEHP, Glyphosate, Pyrene, IPBC, Benzene)

Dansk sammenfatning

Det voksende fokus på håndtering af miljøfremmede stoffer i afstrømmet regnvand øger nødvendigheden af matematiske modeller som støtte til udvikling og evaluering af strategier til kontrol af regnvandskvalitet. Denne afhandling udforsker og belyser modelleringsmetoder til simulering af stoftransport i regnvandssystemer og støtter dermed udviklingen af forureningsbegrænsende strategier. Dette gøres ved at analysere fire forskningsområder: (i) oplandskarakterisering, (ii) modellering af stofafstrømning, (iii) modellering af regnvandsrensning, og (iv) kombineret af overstående i en integreret model. På grund af de betydelige usikkerheder, der er forbundet med modellering af kvaliteten af regnvandsafstrømning, fremlægges identificering af de vigtigste kilder til usikkerhed (baseret på Global Sensitivitets Analyse - GSA) og kvantificering af usikkerhederne på modellens forudsigelser (baseret på pseudo-Bayesianske metoder, så som Generalized Likelihood Uncertain Estimation - GLUE) som væsentlige elementer i modellering af miljøfremmede stoffer i regnvandsafstrømning. Der fokuseres på uformelle kombinerede likelihood mål, som vægter forskellige output (flow og kvalitets målinger).

Håndtering af de spatialt fordelte kilder til miljøfremmede stoffer kræver en detaljeret karakterisering af oplandet og arealanvendelsen ved brug af Geografiske Informations Systemer (GIS). Analysen udført i afhandlingen, som sammenligner forskellige tilgange til oplandskarakterisering med forskellige detaljeringsgrader, tyder på at et højt detaljeringsniveau kan medvirke til identifikation af de vigtigste forureningskilder (og kilder til usikkerheder) i oplandet og dermed danne grundlag for udvikling af kilde kontrol strategier.

Afhandlingen viser hvordan konceptuelle dynamiske modeller kombineret med usikkerhedsanalyse kan bruges til at estimere afstrømning af miljøfremmede stoffer i forbindelse med scenarie analyser. Kombinationen af GSA med usikkerhedsanalyse gør det muligt at identificere interaktioner mellem model faktorer, hvilket ofte ignoreres af traditionelle metoder. Analysen udført i afhandlingen viser, hvordan forskellige uformelle *likelihood* mål i GLUE kan påvirke vurdering af usikkerhederne ved modellens forudsigelser og følgelig anvendelsen af modellerne indenfor regnvandshåndtering.

Skæbnen af miljøfremmede stoffer (opløst og partikulært) i regnvands renseanlæg simuleres ved at kombinere en dynamisk multicelle regnvandsrensnings model med miljøskæbne processer, der modelleres ud fra

stoffernes iboende egenskaber. Den udviklede model (STUMP) overfører således koncepter, som normalt bruges i kemisk risikovurdering, til regnvands renseanlæg ved at tilføje en dynamisk repræsentation af systemet. STUMP kan simulere forskellige stoffer (tungmetaller, organiske stoffer) i forskellige typer anlæg (f.eks. bassiner og biofiltre). Usikkerhedsanalysen udført i afhandlingen gør det muligt at identificere de vigtigste kilder til usikkerhed i forskellige renseanlæg, afhængigt af de dominerende miljøskæbne processer. En reduktion af usikkerheden kan opnås med en korrekt beskrivelse af renseanlæggets fysiske karakteristika, hvilket reducerer behovet for feltmålinger af miljøfremmede stoffer.

Afhandling vise hvorledes integration af de undersøgte modeller giver resultater, der kan bruges i udvikling, vurdering, og sammenligning af forskellige strategier til kontrol af miljøfremmede stoffer (f.eks. kilde kontrol eller forbedring af renseanlæg). Kombinationen af den integrerede model med usikkerhedsanalyse klarlægger hvilke data, der er nødvendige for at forbedre scenarieanalyser og forøger pålideligheden af simuleringsresultaterne. Modellerne udviklet og demonstreret i afhandling anvendes på et virkeligt opland til at vurdere forskellige scenarier til reduktion af udledningen af miljøfremmede stoffer til vandmiljøet.

Afhandlingen fremlægger en pålidelig systematik for anvendelse af modeller til beregning af miljøfremmede stoffers transport fra deres kilder, gennem afløbssystemer og regnvandsrenseanlæg og til recipienten. Dette tilfører vigtig viden om miljøfremmede stoffer i regnvandsafstrømning og forsyner de ansvarlige for håndtering af regnvand i byerne med modelleringsværktøjer til brug i forbindelse med håndtering af forurening fra afstrømmende regnvand. Eksempler i denne afhandling fokuserer på tungmetaller (Cu, Zn) og udvalgte organiske stoffer (DEHP, Glyphosate, Pyrene, IPBC, Benzene).

Table of contents

1. Introduction	1
1.1. The elements in stormwater systems	2
1.2. Application of models in stormwater pollution management.....	3
1.3. Aim of the thesis	5
1.4. Thesis outline	5
2. Research questions	7
3. Context and methods.....	11
3.1. Stormwater quality.....	11
3.2. Legal framework.....	15
3.3. Modelling procedure.....	16
3.4. Analysis of model performance.....	18
3.4.1. Identification of influential factors	18
3.4.2. Estimation of model uncertainty.....	23
4. Source characterization	29
4.1. Theoretical background	29
4.2. Analyzed approaches	30
4.2.1. Research objectives	30
4.2.2. Model description.....	31
4.3. Analysis of results.....	33
5. Pollutant release and transport.....	37
5.1. Theoretical background	37
5.2. Developed approach	41
5.2.1. Research objectives	41
5.2.2. Model description.....	42
5.3. Analysis of model performance.....	44
5.3.1. Identification of important model factors.....	45
5.3.2. Uncertainty analysis	47
5.3.3. Uncertainty in model application	52
6. Treatment.....	55
6.1. Theoretical background	55
6.2. Developed approach	59
6.2.1. Research objectives	59
6.2.2. Model description.....	61
6.3. Analysis of model performance.....	64
6.3.1. Identification of important factors.....	65
6.3.2. Uncertainty analysis	68
7. Integrated models	73
7.1. Theoretical background	73
7.2. Developed approach	73
7.2.1. Research objectives	73
7.2.2. Model description.....	74
7.3. Analysis of model performance.....	75
7.3.1. Uncertainty analysis	75

7.3.2. Uncertainty analysis in model application.....	77
8. Discussion	83
9. Conclusions	87
10. Suggestions for future work	89
11. References.....	93
Appendices	105

1. Introduction

Stormwater quality management is an issue of increasing concern on urban water managers' agenda. The successes in reducing the acute and long-term negative impacts caused by point sources (e.g. wastewater discharge) have increased the attention to chronic impacts and diffuse sources affecting stormwater quality.

Furthermore, recent environmental legislations (e.g. the EU Water Framework Directive (WFD) (European Commission, 2000) and the Environmental Quality Standard (EQS) directive (European Commission, 2008)) identify a wide range of substances (heavy metals, polyaromatic hydrocarbons, herbicides and other xenobiotic organic compounds – commonly named Micro Pollutants - MP) that need to be considered to achieve a good ecological status of natural waters. The focus has thus moved from addressing only traditional “macro” pollutants (overall organic matter, nutrients, suspended solids) to include also micropollutants. While the first are characterized by relatively high concentrations (in the level of mg/l) as well as acute and short time effects (e.g. oxygen depletion, eutrophication), the latter are commonly found in low concentrations (in the level of ng/l – µg/l) and mainly have chronic and long-term impacts on the natural environment. The fate of these substances in the environment can significantly differ from the behaviour of macro pollutants, and therefore the scientific tools that were developed to address macropollutants may be inadequate to deal with MP.

Urban water managers should develop and implement strategies to reduce the non wanted biological impact due to discharge of stormwater MP. These actions require identification of the most critical and representative pollutants (also defined as Priority Pollutants – PP) and the quantification of the fluxes of these substances in stormwater systems. While there are examples of tools developed to select PP (see e.g. Eriksson et al., 2005; Baun et al., 2006), mathematical tools capable of estimating the dynamic fluxes of these specific pollutants in stormwater systems are lacking.

Also, the implementation of extensive monitoring campaigns is limited by the complexity of the system, the high variability of stormwater pollution processes, the difficulties in measuring the low MP concentrations, and problems related to obtaining representative quality data. These limitations boost the role of mathematical models in integrating the monitoring data, providing a complete overview of the situation in the system and evaluating the effects of possible

modifications. Mathematical models can thus provide an important support in the control of stormwater micropollutants, but need to be specifically adapted to the characteristics of these substances.

1.1. The elements in stormwater systems

Separate stormwater systems can be subdivided into three basic parts: the catchment where runoff is generated and sources of pollutants are located, the drainage system which collects and routes stormwater away from the catchment, and, where adopted, a final treatment before discharge into the receiving water. Stormwater quality models can be structured with a similar scheme (Figure 1.1), as described by Ball et al. (1998). Pollutant sources and pollutant generation processes (accumulation on the catchment surfaces) are modelled by specific submodels. Pollutant release processes are modelled by collection submodels, which also estimate the stormwater volume entering the drainage system. Stormwater and pollutant flows are routed across the catchment by transport submodels. Finally, stormwater treatment before discharge in receiving waters is simulated by disposal models.

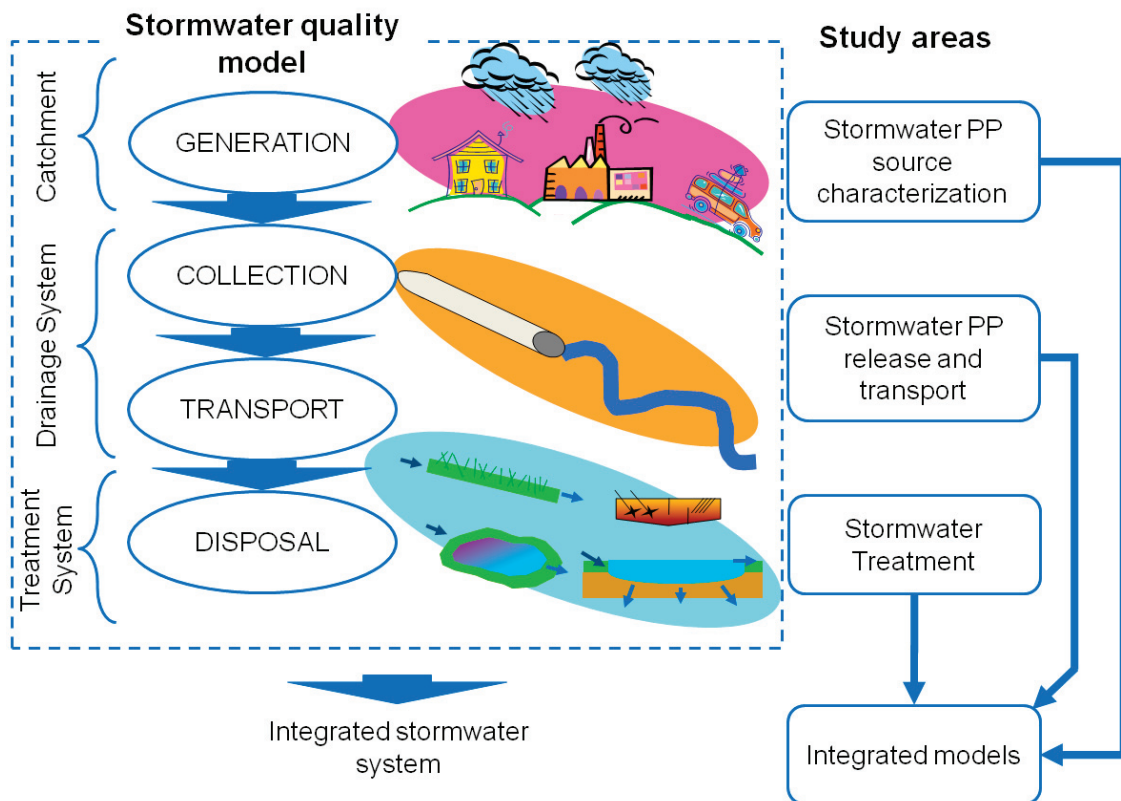


Figure 1.1. Schematization of stormwater quality models (adapted from Ball et al., 1998) and study areas investigated during the project.

The stormwater system is subdivided and studied in this thesis into three areas (exemplified by the three coloured circles in Figure 1.1): the first study area deals with (i) source characterization, the second with (ii) modelling of pollution release and transport and the third with (iii) stormwater treatment. The outcomes from these three study areas are finally combined into an integrated model.

1.2. Application of models in stormwater pollution management

The issues and policies involved in the management of stormwater pollution and the interaction between the various elements of the stormwater system can be described by using the Driver-Pressure-State-Impact-Response (DPSIR - EEA, 1999) framework, which enables an easy delineation of environmental systems and issues. Using this framework, the issues related to stormwater pollution management can be classified as shown in Figure 1.2. Models can play an important role in several phases of stormwater management:

- *Drivers.* Rainfall is the natural process that leads to runoff, while the urban activities that are present within the catchment are potential pollutant sources. Models can be used to estimate the stormwater volume generated in the catchment and to identify the major potential pollutant sources by analyzing the catchment.
- *Pressures.* Priority Pollutants are released from sources, enter stormwater and are transported in the drainage systems. Models can be used to quantify these releases and the loads entering the aquatic environment.
- *State.* Stormwater quality is the environmental variable that expresses the situation in the analyzed system. Models can be employed to estimate stormwater quality, to integrate field measurement in the assessment of the environmental status and to evaluate the effects of stormwater discharge (which are estimated, for example, from simulations of concentrations in the outlet and in the receiving waters).
- *Impact.* Stormwater discharges can have negative effects on the receiving aquatic environment. When dealing with Priority Pollutants, negative effects include acute and other non- time biological limited effects (endocrine disruption, cancer, etc.). Models can be employed to highlight potential problems (e.g. excessive concentrations) and to estimate the temporal scale of such impacts (e.g. frequency and duration of exposure to excessive concentrations).

■ *Response.* Different control strategies can be employed to improve stormwater quality and to reduce the impact on the water environment. Source control options target the Drivers (e.g. substitution of building materials reduces the sources that can release PP) and Pressures (e.g. stormwater infiltration reduces the PP release to the drainage system). Other more technological approaches focus on stormwater treatment, reducing the emissions to the drainage network and to the receiving water. These options contribute to improve the state of the receiving water bodies. Models can be used for scenario analysis, assessing the efficiency of different pollution control strategies by simulating the changes in the PP fluxes across the system and the improvement of the state of the system caused by the implementation of the strategy.

The role of models in the management of stormwater Priority Pollutants is magnified by the difficulties in monitoring these substances and by the complexity of stormwater systems (due to spatial and temporal variability of pollutant sources, hydraulics of the drainage system, etc.). Models can in fact supply information (e.g. long term statistics, data regarding non-monitored events) that can integrate the (commonly limited) monitoring data in the elaboration and assessment of stormwater quality management plans.

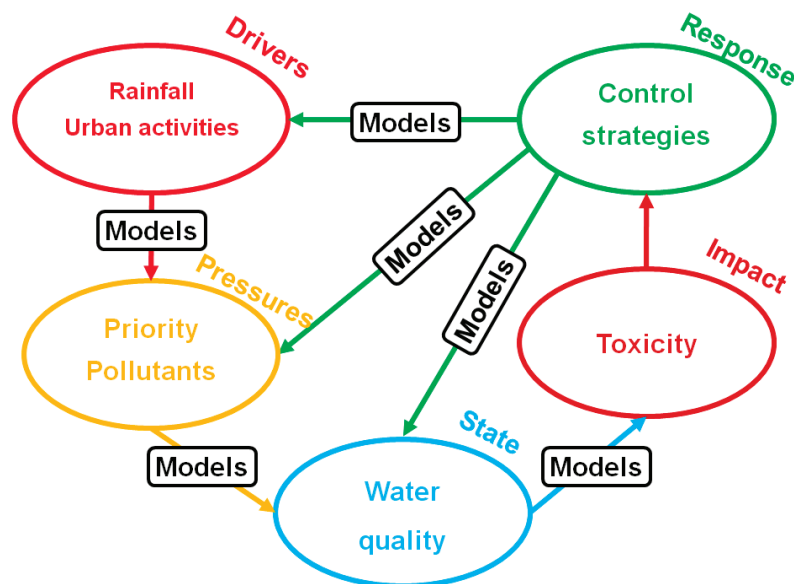


Figure 1.2. DPSIR scheme for the emission of stormwater pollutants to the water environment.

1.3. Aim of the thesis

This thesis aims to provide a framework for the trustworthy application of models to estimate the fluxes of Priority Pollutants across integrated stormwater systems from the source to the sink. These models can provide support in the development and evaluation of policies aiming to control emissions of stormwater PP to water bodies. The thesis investigates the application of models in the various contexts within the elements of the stormwater system described in the previous sections. For each element of the stormwater system listed in Section 1.1, the project aims to (a) identify the available modelling tools, their range of applicability and limitations with special focus on Priority Pollutants. When these tools are not available, (b) new tools are developed. Finally, the analyzed models are tested on real case studies, (c) assessing the model performance against measurements in terms of support for stormwater quality management.

The thesis is based on the main hypothesis that a detailed estimation of PP fluxes in stormwater systems requires dynamic models capable of simulating the system over long time intervals. This is necessary due to the dynamics of the processes involved in stormwater pollution. These dynamic models can be integrated to provide support for stormwater quality management. The latter requires the analysis of highly spatially heterogeneous systems: in the thesis it is thus hypothesized that the pollutant sources in the catchment need to be characterized by using the information stored in Geographical Information Systems (GIS). Given the diverse properties of stormwater micropollutants, it is furthermore assumed that the different chemical properties of the modelled substances should be considered to estimate their fate in the environment. Finally, models are simplifications of reality; therefore a final assumption that is considered through the entire thesis asserts that model results cannot be employed for practical purpose without considering their uncertainty.

1.4. Thesis outline

Section 2 illustrates the research questions that are investigated in the thesis. After an introduction of the general context and methods employed during the project (Section 3), the thesis is structured to resemble the pollutant flow across the stormwater system. The thesis deals with the characterization of stormwater pollutant sources (Section 4), models for the generation and transport of stormwater pollutants (Section 5), and stormwater treatment (Section 6).

For each of the stormwater system elements the questions listed in Section 2 are addressed: by describing (a) the existing knowledge and (b) the models that have been considered/developed during the project; and by (c) assessing the model's performances. Finally, the various parts of the stormwater systems are considered and holistically modelled in Section 7, showing an example of model application in stormwater quality management. The main results of the project and areas for future research are discussed in Section 8 and conclusions are drawn in Section 9.

2. Research questions


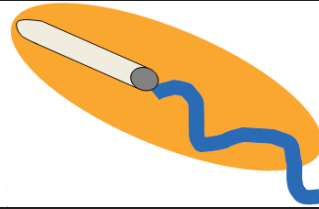
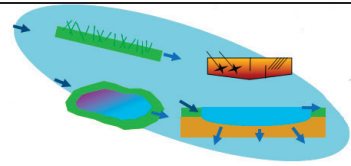
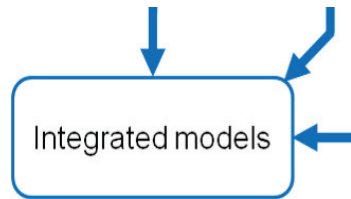
To achieve the objectives of the thesis stated in the previous section, a modeller needs to investigate various issues that can be linked to basic research questions. These questions are addressed in the different sections of this thesis (see the scheme outlined in Table 2.1):

- *How can pollutant sources be characterized? How can the distribution of micropollutant sources across the catchment be represented?*
- *Is it possible to simulate the complex dynamic processes that drive the release of micropollutants into stormwater and their transport across the stormwater system?*
- *What are the fate processes that should be considered to quantify the PP removal in stormwater treatment systems? How can these processes be modelled in different stormwater treatment systems?*
- *How can PP fluxes across stormwater systems be modelled?*
- *Is it possible to simulate the effects of potential pollution control strategies on the existing system? Which information is sufficient?*

While formulating well documented responses to those questions, the following common principles guided the development of the thesis:

- *Expansion of existing models:* several stormwater quality models have been developed in the past decades. There is a solid modelling background to dynamically represent the hydraulic and pollution generation and transport processes in stormwater (limited to macropollutants). Also, several mathematical approaches are available to describe the fate of micropollutants based on their chemical properties. This existing knowledge provides an essential starting point for the development of models that specifically target stormwater PP.

Table 2.1. Outline of the research questions addressed in the thesis.

Catchment characterization			
How can pollutant sources be characterized? How can the distribution of micropollutant sources across the catchment be represented?			
Objectives	Thesis section	Appendices	
Identification of existing models	Section 4.1		
Assessment of performance	Section 4.3		
Pollution release and transport			
Is it possible to simulate the complex dynamic processes that drive the release of micropollutants into stormwater and their transport across the stormwater system?			
Objectives	Thesis section	Appendices	
Identification of existing models	Section 5.1		
Development of model	Section 5.2	Paper I	
Assessment of performance	Section 5.3	Paper I	
Treatment			
What are the fate processes that should be considered to quantify the PP removal in stormwater treatment systems? How can these processes be modelled in different stormwater treatment systems?			
Objectives	Thesis section	Appendices	
Identification of existing models	Section 6.1	Paper II	
Development of model	Section 6.2	Paper II	
Assessment of performance	Section 6.3	Paper III Paper IV	
Integrated system			
How can PP fluxes across stormwater systems be modelled? Is it possible to simulate the effects of potential pollution control strategies on the existing situation? Which information is sufficient? Which additional data are needed?			
Objectives	Thesis section	Appendices	
Assessment of performance	Section 7	Paper IV	

- *Comparison of different modelling approaches*: different modelling tools are available in the literature. These are based on different conceptual approaches that need to be compared (looking at their range of applicability and limitations) when identifying the most appropriate model to simulate PP fluxes in stormwater systems.
- *Evaluation of the appropriate model complexity*: the complexity of the various available approaches needs to be considered in view of the general scarcity of available measurements regarding stormwater quality, and in particular stormwater PP. The chosen level of complexity should be a compromise between the need for a detailed description of the pollution processes, the performance of the model, and the data and resources (computational and modeller's time) availability.
- *Assessment of result uncertainty*: stormwater quality modelling is intrinsically affected by various sources of uncertainty that need to be considered when looking at modelling results. Identification of uncertainty sources and quantification of uncertainty is thus an essential and crucial step to provide reliable and trustworthy results that can be applied in real cases.
- *Flexibility of developed models*: stormwater quality management is a wide field that includes a broad range of substances, release processes and control strategies. Models aiming to support management of stormwater PP needs to be easily and promptly adaptable to the different scenarios that need to be assessed (e.g. different substances, control strategies, etc.).
- *Exploitation of available data*: the general scarcity of measurements regarding stormwater PP may represent an important barrier to model application. Models can provide useful information without field measurements (as commonly done, for example, in the chemical risk modelling field), but their results becomes more reliable when they are combined with field observations. The developed models should thus be able to benefit from all the available data (e.g. flow measurements, data regarding other water quality parameters) in order to improve the reliability of the results in situations characterized by a significant level of uncertainty.

- The knowledge about substance's inherent chemical properties (tendency to sorb, biodegradability, volatility, etc.) may often be the only available information for a wide range of stormwater MP, and these properties thus represent an obvious starting point for models targeting these substances.

These common principles ensure that the presented models represent optimal state-of-the-art solutions, allowing their application in stormwater quality management.

3. Context and methods

3.1. Stormwater quality

Stormwater pollutants

Stormwater quality depends on the environmental media and surfaces that the runoff is in contact with. Rainwater additionally contains substances from long distance atmospheric transport or scavenged from the atmosphere above urban areas. The runoff generated during rain events flows across the urban surfaces, where different substances are released and/or removed by runoff. The substances that can be identified in stormwater, their concentrations and their loads may vary significantly depending on the land use, the human activities and the materials used in the catchment area (Figure 3.1). Stormwater pollution is thus characterized by significant spatial variability across urban catchments.

The concentrations of stormwater pollutants are commonly lower than in domestic wastewater (see some examples of stormwater concentration values in Göbel et al., 2007), so that discharge of stormwater micropollutants rarely causes acute effects on the receiving aquatic environment.

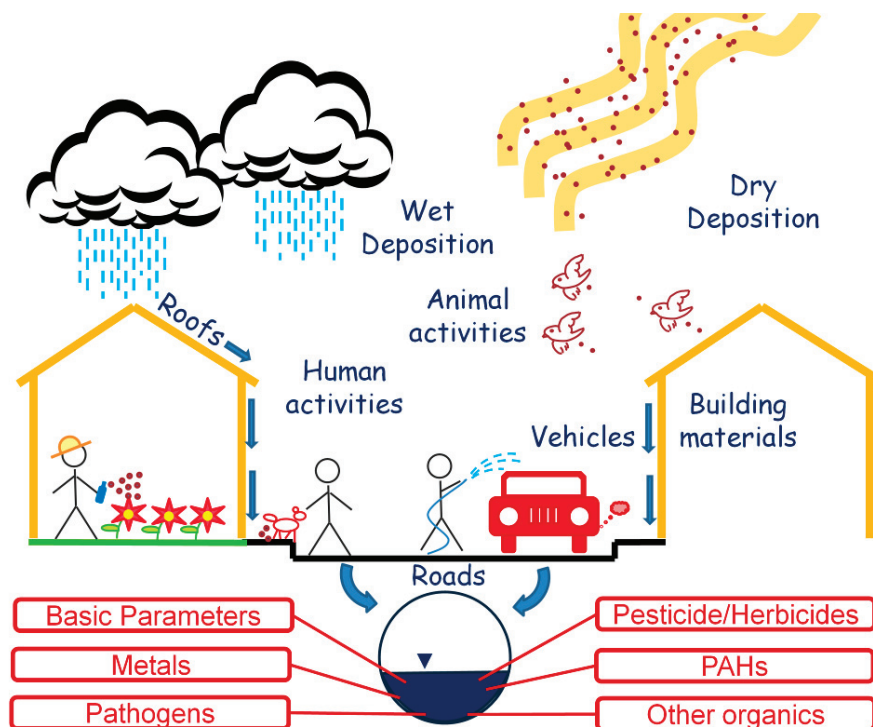


Figure 3.1. Scheme of major stormwater pollutant sources in urban areas and main group of water quality parameters.

Nevertheless, as shown in Figure 3.2 stormwater from urban areas can cause long-term effects (as documented by toxicity studies performed by e.g. Kayhanian et al., 2008; McQueen et al., 2010) and negatively impact the quality of natural ecosystems (e.g. Eriksson et al., 2007; Karlaviciene et al., 2009).

Stormwater quality monitoring

The stochastic nature of precipitation influences the temporal behaviour of stormwater pollution, which is also affected by the temporal emission pattern of the various sources. These factors generate a high temporal variability in the concentrations and loads in stormwater, which is very difficult to monitor. In fact, extensive sampling is needed to obtain a detailed and reliable description of the pollutants' behaviour during a rain event. Depending on the equipment (e.g. the volume collected) and the sampling technique (e.g. flow proportional or time proportional sampling), the data regarding stormwater quality can describe stormwater pollutographs with different levels of detail.

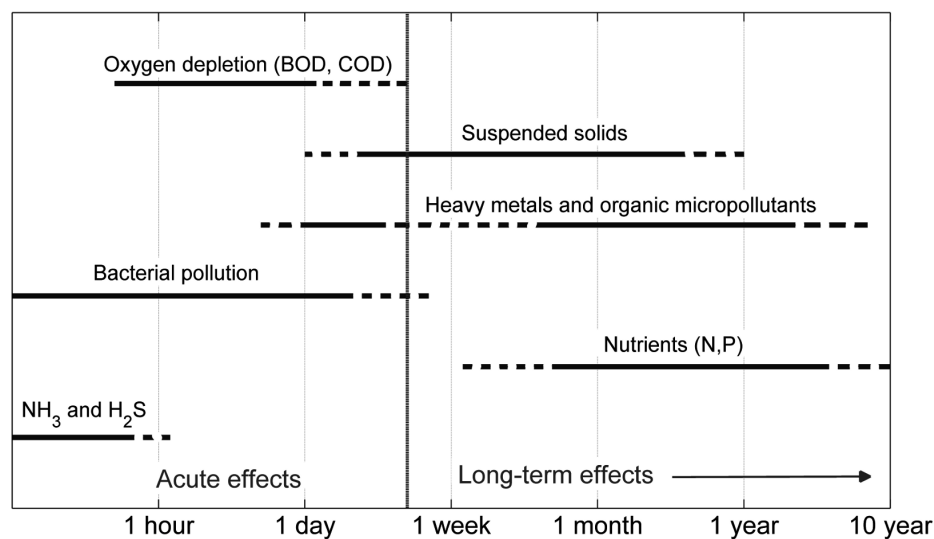


Figure 3.2. Time scale for effects caused by stormwater discharge: stormwater priority substances can cause both acute and long-term toxicity (from Hvitved-Jacobsen et al., 1994).

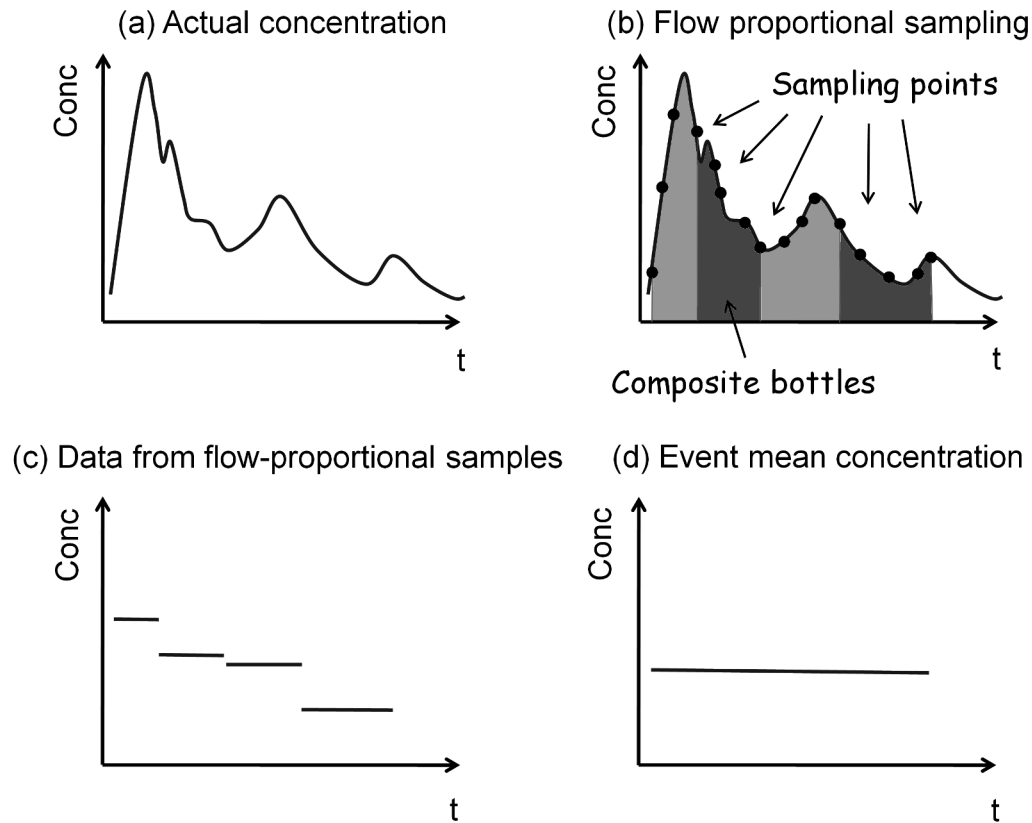


Figure 3.3. Representation of concentration data from the actual concentration down to the Event Mean Concentration obtained through a flow proportional sampling procedure.

Figure 3.3 exemplifies the data collection process for a flow-proportional sampler: the actual stormwater concentration (a) is sampled at discrete intervals and collected in composite sample bottles (b). Samples from these bottles are analyzed and it is possible to reconstruct a pollutograph (c) or to integrate the measured concentrations with the flow data and calculate the Event Mean Concentration (EMC) (d). The latter is calculated as the ratio between the total mass discharged during the event and the total event volume.

From measurements collected during separate rain events it is possible to calculate the Site Mean Concentration (SMC) as the ratio between the total mass and volume discharged during several events, which provides information about the stormwater quality in the study site over long time periods.

Table 3.1. Summary of stormwater quality data used in the thesis.

Location	Sampling technique	Data resolution ^b	Sampling period	Spatial data	Area [ha] ^e	Catchment		Section							Paper					
						Usage	Treatment	4	5	6	7	I	II	III		IV	V			
Basin K, Albertslund, (Denmark)	FP ^c - TP ^d	Pollutograph (33 ^c – 14 ^d)	May-October 2010 (5 events)	GIS, aerial photo	92	Industrial/ Residential	Retention pond	X			X									X
Vasastaden, Göteborg ^f , (Sweden)	FP	Pollutograph (57)	April-May 2002 (13 events)	GIS, aerial photo	4.8	Residential	None	X	X			X								
Monash University, Melbourne, (Australia) ^g	FP	Pollutograph (31 ^c – 38 ^d)	February-March 2007 (3 events)	Map	0.45	Parking	Biofilter			X										X
Skullerød, Oslo, (Norway) ^h	FP	Mean concentration (20)	May 2003 – May 2004	Map	2.2	Highway	Retention pond		X											
Lilla Essingen, Stockholm, (Sweden) ⁱ	FP	Mean concentration (9 ^c – 16 ^d)	May – August 2004	Map	1.2	Highway	Retention pond and filtration			X			X	X	X					X

^aFP: Flow Proportional; TP: Time Proportional; ^bPollutograph: samples subdivided per rain event. Mean concentration: volume weighted mean concentrations covering several rain events. Number of samples listed in brackets; ^cInlet to the treatment unit; ^dOutlet from the treatment unit; ^eImpervious area. ^fDescribed in Ahlman (2006). ^gDescribed in Hatt al. (2009a; b). ^hDescribed in Vollertsen et al. (2009). ⁱDescribed in Stockholm Vatten (2006).

Clearly, the information provided by samples is an approximation of reality. While trying to reproduce reality, the modeller needs to consider that observations may not be as detailed as the model would require. For example, a dynamic model can generate continuous concentration data (reproducing the natural pattern in (a)) that, however, can only be compared against the measurements from bottle samples (c) or event-based data (d).

This inherent data uncertainty needs to be considered when selecting the level of detail of the model and when trying to quantify model uncertainty. In fact, the models developed in this thesis are evaluated against data collected with different sampling techniques (see Table 3.1).

3.2. Legal framework

Pollution caused by stormwater discharge is covered by the EU Water Framework Directive (WFD) 2000/60/EC (European Commission, 2000). The WFD does not define precise technical requirements, but provides guidelines for water quality management at the catchment level. This should be based on the application of the Best Available Technologies and on establishing Best Environmental Practices. A major objective of the WFD is the enhancement of the status of the aquatic ecosystems through the progressive reduction of discharges, emissions and loss of Priority Substances (PS) and the cessation or phasing-out of discharges, emissions and losses of Priority Hazardous Substances (PHS).

Among the criteria for a good ecological status, the directive lists the Environmental Quality Standards (EQS), which define the maximum concentrations of PS in water (defined as maximum allowable – MAC, and annual average – AA), sediments and biota. EQS are further defined in the WFD daughter directive 2008/105/EC (European Commission, 2008) on Environmental Quality Standards. A great number of the substances listed in the directives can be identified in stormwater from urban areas. The fulfilment of the WFD water quality objectives thus requires the consideration of PS loads discharged by stormwater.

Depending on the considered spatial scale, stormwater discharges can either be regarded as point or diffuse sources, which are both regulated through the implementation of *emission control strategies*. These are defined as a combination of emission limitations (e.g. limits on the mass/concentration

emission) or activities affecting the emission processes (e.g. source control, end-of-pipe treatments, etc.). Emission control strategies should be cost-effective and proportional: this thus requires the assessment and comparison of different control strategies. Models can provide results that support the identification of the most appropriate emission control strategy for a specific area.

The EQS directive 2008/105/EC also introduces the concept of mixing zones, which are areas in proximity of the discharge point where exceedance of EQS for one or more PP is allowed, given that this does not affect the compliance of the rest of the water body with those standards.

The compliance of stormwater discharge with the EQS requirements might potentially be assessed through the application of models (e.g. Gevaert et al., 2009; Bach et al., 2010; Mouratiadou et al., 2010; Yang and Wang, 2010).

3.3. Modelling procedure

The implementation and application of models can be subdivided into general steps (see for example the schemes presented in Carstensen et al., 1997; Jørgensen and Bendoricchio, 2001; Dochain and Vanrolleghem, 2001; Jakeman et al., 2006; Refsgaard et al., 2007) where some can be neglected according to specific situations (e.g. when a model is available, a modeller can directly jump from the problem formulation to the model diagnosis). Hereafter a short description of the various phases of model development that are performed in the thesis is presented (Figure 3.4).

The starting point for the application of a model is the definition of the goal (e.g. improved quality of natural waters) and the formulation of the questions that the modeller should answer (defined in Section 2). Once clear objectives are defined, relevant knowledge can be identified in the available literature. This information can highlight relevant experiences and tools to solve the defined problem (e.g. existing models, as described in Section 5.1 and 6.1).

The model formulation and implementation represents the core of the process of model development. In this phase the general conditions under which the model operates (e.g. main assumptions) are outlined, the model structure and equations are selected and model parameters and the variables are defined (an example of this step is the development of the treatment model presented in **Paper II**). The model is then coded in the programming language and software selected according to the choices made during model formulation.

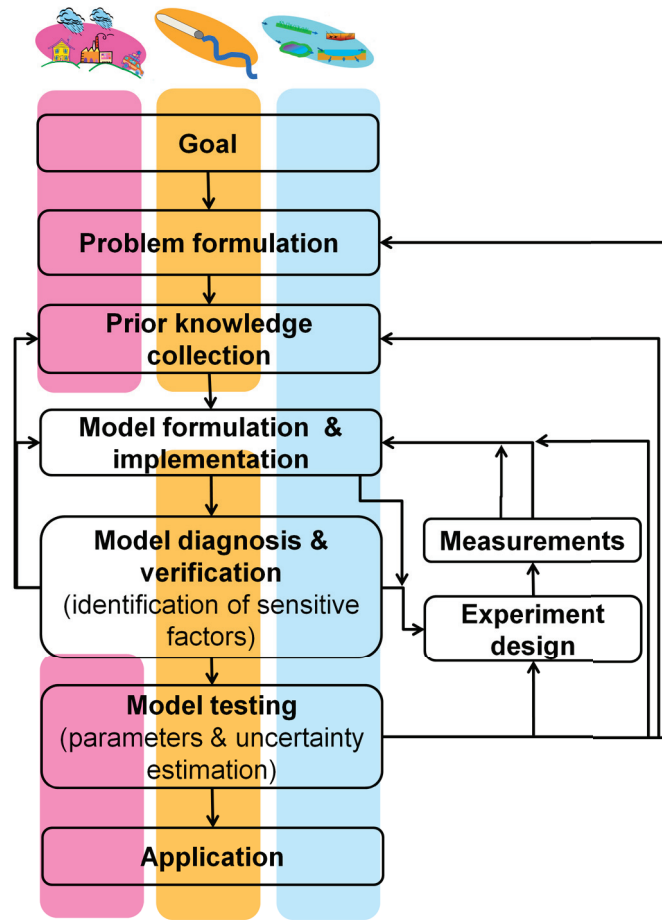


Figure 3.4. Procedure for model building (adapted from Carstensen et al., 1997; Jakeman et al., 2006; Refsgaard et al., 2007). The coloured areas represent the steps performed in the project for each element of the stormwater system.

Dynamic models (as the one presented in Section 5.2.2) require software with proper numerical solvers. The use in integrated models should use platforms that facilitate integration with other models (e.g. MATLAB/SIMULINK[®], used in **Paper V**, or WEST[®], used for the stormwater treatment model - **Paper II, III** – and its integration with other models (De Keyser et al., 2010)).

Once the model is implemented, its behaviour is analyzed and problems, weak points, and areas of improvements are diagnosed. This phase is also commonly defined as sensitivity analysis (Saltelli, 2000) and it helps the modeller to (i) identify the most influential and significant model factors (i.e. parameters, inputs, variables) with respect to the model output, (ii) detect potential interactions between the model factors and (iii) highlight regions of the parameter space that ensure optimal results. The results of the sensitivity analysis may motivate further studies and/or model re-formulation and provide the basis for the

definition of the data needed to assess the performances of the model. An example of the results from this stage can be found in **Paper I** and **Paper III**.

Subsequently the model is tested and its performance is analyzed by comparing its results against measurements. This stage includes the estimation of the parameters that ensure better performance (this phase is also defined as calibration and some examples are presented in **Paper I** and **IV**). The evaluation of the model also involves the quantification of the result uncertainty and the testing against additional measurements (defined as validation, corroboration or confirmation). These last stages are essential to increase the confidence in the model before its final application and are illustrated in detail in the following section.

3.4. Analysis of model performance

For a trustworthy application of models a comprehensive knowledge of the model performance is necessary. The modeller should be aware of the most influential model factors for the model outputs and their interactions. This allows the identification of the major sources of uncertainty, i.e. the areas where resources need to be focused to improve the model performance (Saltelli and Annoni, 2010).

Models are a simplification of reality and multiple sources of uncertainty (inputs, parameters, model structure, and measurements) make it impossible to exactly simulate reality. The model results thus need to undergo an uncertainty analysis, i.e. uncertainty bounds should quantify the level of confidence in the results. Although this is valid for any field of environmental modelling, uncertainty analysis is crucial when dealing with stormwater pollution. Modelling of stormwater pollution is, in fact, affected by high uncertainty related to the difficulties in monitoring, high variability and complexity of the processes, and difficulties in estimating the model parameters, (Bertrand-Krajewski, 2007).

3.4.1. Identification of influential factors

Sensitivity analysis allows the identification of the major sources of uncertainty without requiring measurements, as the focus is on the model behaviour rather than on its performance. Sensitivity analysis has traditionally been performed by applying “One-At-Time” (OAT) methods (also called local sensitivity analysis), i.e. the response of the model output to the variation of one factor is calculated

for each single model factor separately. The first-order sensitivity index S_i is then calculated for the i -th model factor X_i according to the formula:

$$S_i = \frac{\frac{\Delta M}{M}}{\frac{\Delta X_i}{X_i}} \quad (3.1)$$

where the numerator expresses the relative variation of the model output M and the denominator defines the relative variation of the model factor X_i . This approach is widely applied for its simplicity and low computational requirements (for a k -dimensional model factor space only k simulations are needed), but it fails to provide a complete overview of the model features (see the complete discussion presented in Saltelli and Annoni, 2010). OAT methods, in fact, provide information on the model behaviour only in a limited region of the model factor space around the starting point of the analysis (Figure 3.5). Also, the fact that model factors are assessed separately entails that OAT fails to identify interactions between factors and thus neglects potential sources of uncertainty.

Several approaches (defined as Global Sensitivity Analysis – GSA - methods) are available to overcome the limitation of OAT methods (Saltelli et al., 2006; Saltelli and Annoni, 2010) and assess the model's behaviour across the entire parameter space. This study focused on the application of the Elementary Effects and Variance Decomposition methods.

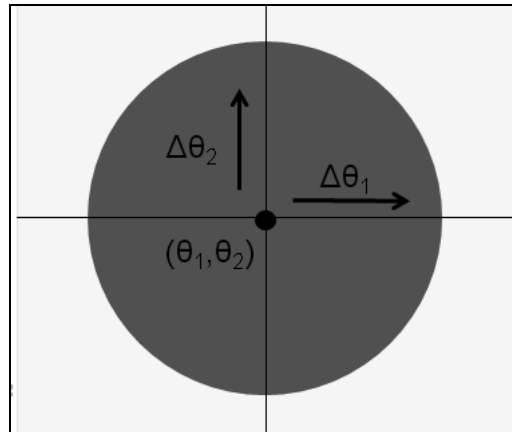


Figure 3.5. Example of the fraction of parameter space explored by OAT methods (dark grey area) for a two factors (θ_1, θ_2) model.

Elementary effect method

The Elementary Effect method (also called the Morris method - Morris, 1991) represents a compromise between the need to explore various regions of the factors space and the computational burden required by highly detailed GSA methods (and it is thus applied in **Paper III** and **IV**).

The Morris method is based on multiple OAT analyses performed in several regions of the factor space. A number of R initial points are generated in the factor space in order to achieve a better coverage of the entire space. Several strategies are proposed to optimize the sampling across the factor space while minimizing the computational burden (Campolongo et al., 2007; Pujol, 2009). These are used as starting point for the development of R trajectories, i.e. for the application of R local analyses (Figure 3.6). For each r -th trajectory first order sensitivity indices $S_i^{(r)}$ are calculated according to Eq. 3.1. The Elementary Effects are the statistics (mean and standard variation) of the sensitivity indices (Campolongo et al., 2007):

$$\mu_{ii}^* = \frac{1}{R} \sum_{r=1}^R |S_i^{(r)}| \quad (3.2)$$

$$\hat{\sigma}_{ii} = \sqrt{\frac{1}{R} \sum_{r=1}^R (S_i^{(r)} - \hat{\mu}_i)^2} \quad (3.3)$$

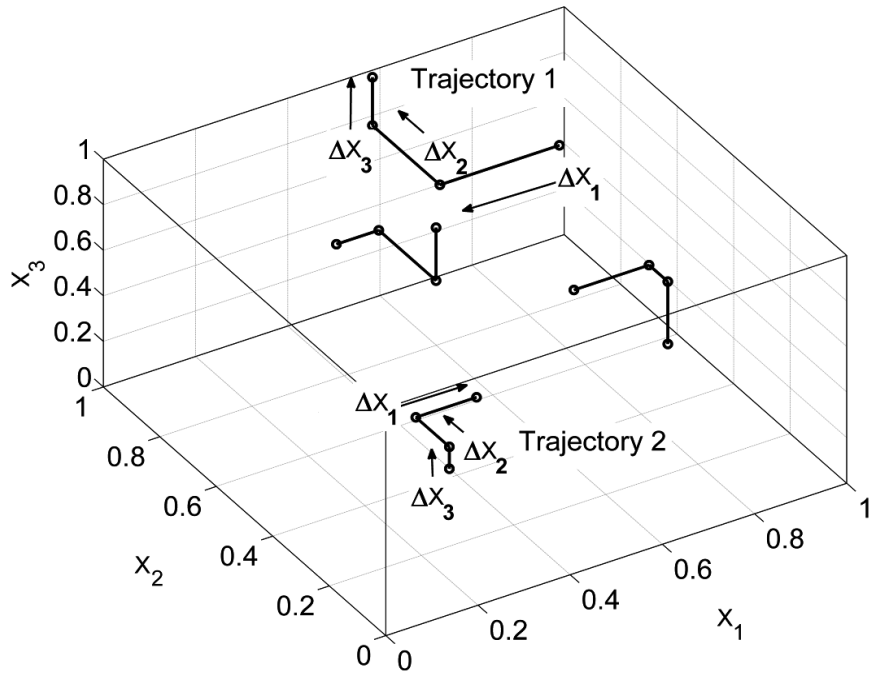


Figure 3.6. Example of four trajectories generated for the Morris method in a three dimensional (X_1, X_2, X_3) factor space (adapted from Pujol, 2009).

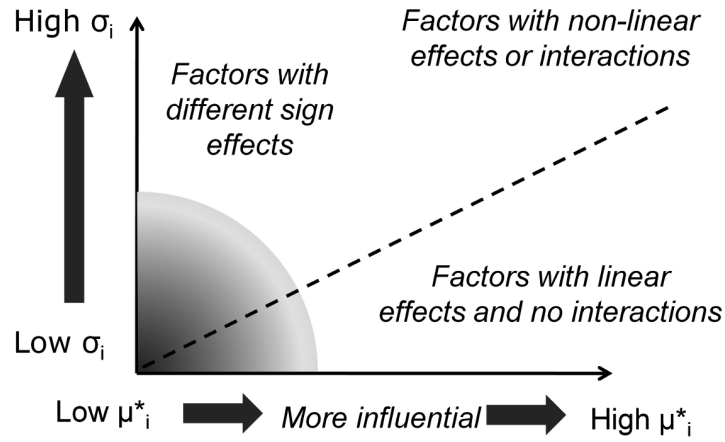


Figure 3.7. Scheme for assessing the influence and behaviour of model factors based on the analysis of elementary effects.

Analysis of the elementary effects (see the scheme in Figure 3.7) enables the identification of factors that have a significant influence on the model outputs and/or interacts with other factors (with negative/positive correlation or correlations that have different effects for different regions of the factor space).

Compared to OAT methods, the analysis of the elementary effects provides a deeper understanding of the internal dynamics of the model. This is obtained with limited computational requirements, as for a k -dimensional model factor space an analysis with R trajectories requires $R \cdot (k+1)$ model runs are required. Campolongo et al. (2007) and Gatelli et al. (2009) showed that the elementary effects can be profitably employed as substitutes for more computationally demanding indices (such as the Sobol' indices – see next section).

Variance decomposition methods

A detailed GSA method that provides a deep insight in the model behaviour is the variance-decomposition method proposed by Sobol' (Chan et al., 2004). The method essentially identifies the contribution to the output variance (V) of each model factor when acting alone or interacting with other model factors.

As the detailed decomposition of the model output variance would be computationally demanding, Sobol' indices are commonly used to reduce the number of calculations (Chan et al., 2004). Sobol' indices are the first order sensitivity indices S_i , which express each factor's direct influence on the output variance, and the total sensitivity indices S_{Ti} that lump all the interactions of the factors into a single value (Figure 3.8).

The two indices are calculated by generating n samples from the factors space for each of the k model factors. The model is run for each sample and the variance V of the model output is calculated. Subsequently, the sample is modified by generating a new sample for the model factor X_i . The model is run again and the new variance V_i is calculated, leading to the estimation of the first-order index according to the formula:

$$S_i = \frac{V_i}{V} \quad (3.4)$$

The original sample is then modified again by generating a new sample for all the factors except i . The output variance is then calculated ($V_{\sim i}$), leading to the estimation of the fraction of variance that is related to all the factors except i :

$$S_{\sim i} = \frac{V_{\sim i}}{V} \quad (3.5)$$

The total variance V (Figure 3.8) is the sum of the variance due exclusively to the model factor X_i (V_i), the variance caused by the interactions between all the factors ($V_{i, \sim i}$) and the variance caused by all the factors except X_i ($V_{\sim i}$):

$$1 = S_i + S_{i, \sim i} + S_{\sim i} \quad (3.6)$$

The total sensitivity index S_{Ti} is then calculated by rearranging Eq. 3.6:

$$S_{Ti} = S_i + S_{i, \sim i} = 1 - S_{\sim i} \quad (3.7)$$

Despite being less computationally demanding than a detailed variance decomposition, the computational burden needed for the estimation of Sobol' indices is higher than for the Elementary Effects method. In fact, for a model with k factors and n samples, $(2*k+1)*n$ model runs are necessary. The dimension of the sample n is a crucial factor, as it should be able to provide a good representation of the model output variance.

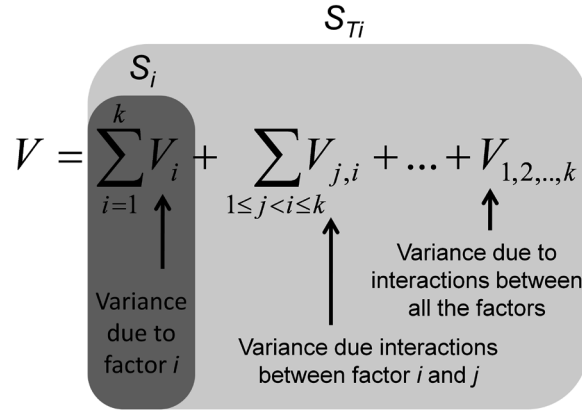


Figure 3.8. Scheme of the information provided by the Sobol' indices.

The example presented in **Paper I**, for example, shows that for a simple conceptual stormwater quality model a sample with dimension $n=100,000$ is not entirely sufficient to achieve a complete overview of the output variance, as negative indices are estimated for factors with almost negligible influence. Variance decomposition methods are thus capable of exactly quantifying the influence of each factor, but are not suitable for models with long simulation time.

3.4.2. Estimation of model uncertainty

The last decade has seen an increasing focus on the estimation of model uncertainty. This is generated by a philosophical shift in the modelling community that acknowledged the limitations of models and recognized the need for quantifying the result's uncertainty. The general mathematical formulation that accounts for model uncertainty is expressed by Eq. 3.8 (adapted from Beven, 2009):

$$O(x,t) + \varepsilon_O(x,t) = M(\theta, \varepsilon_\theta, I, \varepsilon_I, x, t) + \varepsilon_M(\theta, \varepsilon_\theta, I, \varepsilon_I, x, t) \quad (3.8)$$

where O is the observed variable in the real system, ε_O is the observation error, ε_θ is the error of model parameters, ε_I is the error in input and boundary conditions, and ε_M is the model structure error.

There is a great number of available uncertainty analysis methods for environmental modelling (see the review in Matott et al., 2009) that try to infer the model error term ε_M listed in Eq. 3.8. The scientific community has not defined a common framework for the application of uncertainty estimation techniques yet. Nevertheless, the inherent level of uncertainty affecting stormwater quality modelling (Bertrand-Krajewski, 2007) renders uncertainty

analysis essential for a reliable application of such models (an example of how uncertainty can be integrated in stormwater quality management is shown in Section 7.3).

This thesis focuses on the so-called pseudo-Bayesian methods (Freni et al., 2009b), which require a smaller number of *a priori* assumptions than traditional Bayesian approaches. Thanks to this feature they are thus regarded as more suitable for the uncertain field of stormwater quality modelling. The uncertainty analyses performed in this thesis are based on the Generalized Likelihood Uncertainty method (GLUE - Beven and Binley, 1992), which is based on the equifinality thesis (Beven, 2006), i.e. different parameter sets can achieve equally good predictions.

The GLUE method can be summarized in the following steps (Beven, 2009):

1. Definition of an informal (or formal) likelihood measure L , i.e. the measure that is used to evaluate the model performance.
2. Definition of the model parameters and inputs to include in the analysis. This step can benefit from the results of sensitivity analysis.
3. Definition of prior distributions for the analyzed model factors. These are used to generate n parameter sets. The prior distributions are defined according to prior knowledge (e.g. literature values). Uniform distributions are commonly chosen when little information is available.
4. The model is run for each parameter set (Monte Carlo simulations) and the performance of the model is evaluated by using the likelihood measure.
5. The *behavioural* parameter sets are selected according to an acceptance/rejection criterion
6. The output generated by the behavioural parameter sets is used to create model prediction bounds

There is lively debate in the environmental modelling community about the applicability of GLUE (see for example Mantovan and Todini, 2006; Beven et al., 2008; and the comparisons in Freni et al., 2009b; Dotto et al., in preparation; Jin et al., 2010). This discussion deals with the width of the prediction bounds, namely on the mathematical significance of the estimated model prediction bounds, the posterior parameter distributions, etc. This study does not address

these aspects, but focuses on some aspects of the GLUE methodology (choice of the likelihood measure and generation of the parameter sample).

Likelihood measures

The GLUE methodology assesses the model performances by using informal (or formal) likelihood measures (Beven and Freer, 2001). Commonly, these measures are based on the deviation between simulated and measured data (which is commonly assumed to have no error - e.g. Eq. 3.9 and 3.10), but new measures have been proposed to reproduce measurements error (e.g. fuzzy membership functions - Beven, 2009).

A widely applied informal likelihood measure is based on the inverse of the error variance σ_i^2 :

$$L[M(\theta_i|I,O)] = \left(\frac{1}{\sigma_i^2} \right)^N \quad (3.9)$$

where L is the informal likelihood of the model output M estimated for the parameter set θ_i , conditional the input I and the observations O . The coefficient N can be used to sharpen the likelihood response surface and to emphasize the distinction between behavioural and not behavioural parameter sets (Beven and Freer, 2001). Another measure is based on the Nash-Sutcliffe coefficient (Smith et al., 2008), widely applied in hydrological field due to its easy interpretation, as the perfect model provides an index equal to 1:

$$L[M(\theta_i|I,O)] = \left(1 - \frac{\sigma_i^2}{\sigma_{obs}^2} \right)^N \quad (3.10)$$

where σ_{obs}^2 is the variance of the observed values. The advantages and limitations of some likelihood measures have been investigated in **Paper I**. Eq. 3.10, for example, is not suitable for small datasets with significant internal variability, such as pollutographs. For these data, the variance based equation (Eq. 3.9) is more appropriate.

The flexibility of the GLUE methodology allows the use and the combination of different informal likelihoods (see Beven and Freer, 2001) that can be defined according to model, system and observations characteristics. The combination used in the thesis is based on a weighted average of likelihood measures L (Eq. 3.11) for different outputs M_1, M_2, \dots, M_k . The weights $\omega_1, \omega_2, \dots, \omega_k$ express the relevance that each factor has for the modeller.

$$L_{combined} = \omega_{M_1} L_{M_1} + \omega_{M_{12}} L_{M_{12}} + \dots + \omega_{M_k} L_{M_{1k}} \quad (3.11)$$

Examples of these combinations can be found in **Paper IV** (likelihood on TSS and Cu concentrations, and on simulated flow and total volume). These examples illustrate how modellers can choose different likelihood measures (or combination hereof) depending on the model outputs they are interested in. Compared to other uncertainty analysis techniques (e.g. Bayesian) this feature allows modellers a wider degree of freedom.

Parameter sample generation

The application of uncertainty analysis techniques (including GLUE) requires the assessment of model performances by using a great number of parameter sets generated across the parameter space. The computational burden can represent a significant obstacle to the estimation of model results uncertainty, especially for complex model and long simulation time. To reduce the computational requirements of GLUE in this thesis, this technique is combined with the Shuffled Complex Evolution Metropolis algorithm (SCEM-UA - Vrugt et al., 2003). This optimization algorithm identifies the region in the parameter space with higher likelihood, i.e. the parameter sets that provide better performances. The application of the SCEM-UA in conjunction with GLUE was initially developed by Blasone et al. (2008a; 2008b) and applied in stormwater modelling by Lindblom et al. (2007a).

In stormwater quality modelling, where the uncertainty linked to parameter distributions is significant, the SCEM-UA can contribute to reduce the computational requirements. The significant level of parameter uncertainty (sometimes resembling ignorance) requires the use of wide parameter distributions to generate the parameter sets. Obtaining a sufficient sampling density across the entire parameter space with random methods (including Latin hypercube sampling) would require a great number of samples, while the SCEM-UA starts from a low-density sample (Figure 3.9a) and subsequently concentrates the parameter sets in the higher likelihood regions (Figure 3.9b).

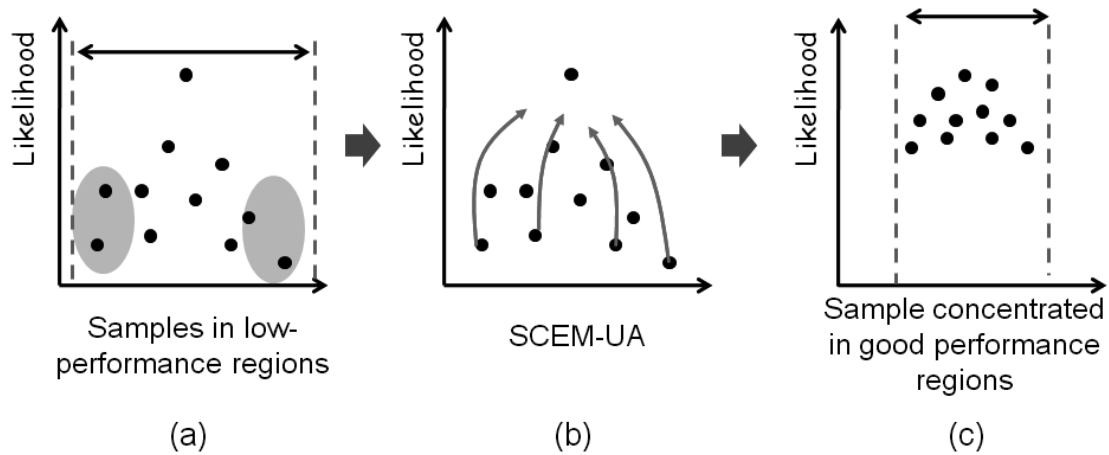


Figure 3.9. Scheme of the application of the SCEM-UA algorithm to improve the parameter sample performance: the algorithm moves the samples generated from wide parameter intervals (a) towards the regions ensuring better performances (b), generating the sample for the subsequent GLUE analysis (c).

This generates a sample with high density only in the regions of the parameter space providing good model performances (Figure 3.9c). This sample can subsequently be used to run the GLUE analysis.

In **Appendix VII** it is shown how the application of the SCEM-UA can result in up to 70% saving of computational resources compared to random sampling methods. When compared with other uncertainty estimation methods (Dotto et al., in preparation), the SCEM-UA provided similar results in terms of prediction bounds and parameters distribution with lower computational requirements. The combination of SCEM-UA with GLUE thus represents a significant improvement of efficiency in uncertainty analysis in stormwater quality modelling.

4. Source characterization

4.1. Theoretical background

Stormwater quality depends on the pollutant sources in the catchment. The identification of potential PP sources in the area of interest is the first step to model PP in stormwater systems. The characterization of catchments and pollutant sources is commonly performed by utilization of Geographical Information Systems (GIS), which provide support in the management of spatial information about the study area and potential PP sources (e.g. land usage, location of streets, etc.).

Stormwater pollutant loads are calculated by coupling hydrological models with PP release data (measured or retrieved from databases). This information can either be expressed as average concentrations (e.g. Site Mean Concentration) or as release factors. In the first case the PP loads are function of the runoff volume, while in the latter they are function of time or of the unit used to quantify the PP source (e.g. km driven for PP released by traffic). Other factors affecting the detail level of the catchment descriptions are the substances investigated, the size of the catchment, the desired output of the model (load or concentration) and the purpose of the model application (e.g. compliance with discharge limits - concentrations or loads).

The estimation of stormwater pollutant loads from large catchments may require a lumped description of the area, commonly based on land usage (for example Park et al., 2008; Park and Stenstrom, 2009). The characterization of land usage can rely on available data or can automatically be performed from aerial observations (Park and Stenstrom, 2009; for example, presented examples based on satellite imagery). The combination of land usage information with average concentration data extends the approach commonly used at the river basin scale for pollutants from agricultural runoff (e.g. the estimation of N and P loads presented by Johnson et al., 2001; or the identification of potential pollution sources for drinking water protection presented by Grayson et al., 2008). The SMC-based methods have widely been applied at the urban scale in the U.S., boosted by the national stormwater legislation (based, for example, on the Total Maximum Daily Loads; see also Park et al., 2008) and by the available SMC databases (see for example Pitt and Maestre, 2005; and Park et al., 2009). These applications mainly cover “traditional” water quality parameters and heavy

metals, with some examples regarding pesticides (Qiu and Prato, 1999; Grayson et al., 2008) and PAH (Mitchell, 2005).

Dynamic models for small catchments may use highly detailed description of the PP sources in the study area (e.g. Ahlman, 2006), but field data collection might be demanding. The initial catchment description based on GIS data, in fact, may require a further refinement to achieve a more precise description of potential PP sources (e.g. copper roofs). This additional investigations can be based on analysis of aerial photos (e.g. Ekstrand et al., 2001) or on site inspections. SMC-based methods are also applied with a detailed characterization of the catchment, as presented by Modaresi et al.(2010).

GIS-based pollutant release models provides results that highlight the most relevant pollution sources (Kim et al., 1993; Mitchell, 2005; Grayson et al., 2008). Economic models for treatment options can furthermore be included in the models and the integration of GIS models in Decision Support Systems (DSS) provides support for the assessment of pollution control strategies (Nordeidet et al., 2004; Hipp et al., 2006; Zheng et al., 2006).

4.2. Analyzed approaches

4.2.1. Research objectives

Various factors contribute to the definition of the approach chosen to characterize and model pollutant sources in a catchment (data availability, size of the catchment, legal requirements that need to be fulfilled). The quality of the results is affected by this choice. The work presented in this thesis aims to compare various approaches that can be used to model PP stormwater sources. The comparison tries to identify the most suitable approaches for modelling of PP fluxes across stormwater systems by considering the spatial distribution of PP sources. This comparison of different catchment characterization methods focuses on the estimation of three heavy metal loads (namely Cd, Cu and Zn), which are chosen for the availability of information, in urban areas.

The study extends the work presented by Park et al. (2009) that investigated the effect of different SMC datasets on the estimated annual loads for a large catchment (over 200 km²). The focus in this thesis is on the level of detail of urban catchment characterization (e.g. in small catchments of few squared kilometres).

4.2.2. Model description

Three approaches for the characterization of a small urban catchment are compared: the first two (A,B) are based on SMC, while the third (C) employs release factors. The three methods differ with respect to the level of detail of catchment characterization, where the first (A) lumps the entire catchment into a single area and the others (B,C) use a detailed representation of the catchment (Table 4.1).

The comparison of different methods is performed for a small urban catchment in Göteborg, Sweden (4,8 ha -see **Paper I** and Ahlman, 2006) and for an industrial-residential catchment in Albertslund, Denmark (about 95 ha - see **Paper V**). These two catchments are selected as the required information is available and thus the application of the different approaches is not limited by data availability. The Göteborg catchment was classified by Ahlman (2006), and the Albertslund catchment was classified in this PhD project based on the information (road and building cartography) provided by the Albertslund municipality.

The catchments are classified by using a combination of GIS data and aerial photos into three impervious areas typologies (for example, see Figure 4.1 for Göteborg): roofs (subdivided into copper, sheet steel and tile roofs), roads and parking lots (areas in contact with motor vehicles), and other impervious areas (e.g. yards and pavements).

Table 4.1. Characteristics of the three approaches for catchment characterization included in the study.

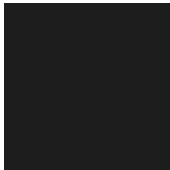
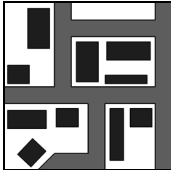
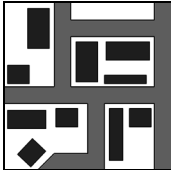
Approach	A	B	C
Detail of classification			
	Lumped	Detailed	Detailed
Classification categories	City centre Residential Industrial	Roof (with identif. of copper and zinc roofs) Roads Other impervious areas	
Pollutants loads estimation	SMC	SMC	Release factors

Table 4.2. Pollutant source data used in the comparison.

Land usage/pollutant sources	Concentration values ^a [µg/l]			Release factors [mg/m ² /year] ^b		
	Cd	Cu	Zn	Cd	Cu	Zn
City centre ^c	0.5 (0.3-0.9)	70 (25-110)	250 (120-400)			
Residential area ^c	0.5 (0.3-0.7)	35 (20-70)	120 (60 -200)			
Industrial area ^c	0.5 (0.3-0.9)	70 (25 -110)	250 (120-400)			
Roads and parking lots ^c	0.5 (0.3-1.0)	75 (25-110)	240 (100-350)	0.150 ^d	4 ^d	15 ^d
Corrosion of zinc surfaces				0.09		4000
Road wearing				0.04 ^e	7 ^e	15.8 ^e
Vehicle emission (tyres, brakes, oil discharge)				0.5 ^e	25 ^e	1500 ^e
Roofs	0.8 (0.1-1) ^f	35 (10-1000) ^f	140 (50-1000) ^f	0.150 ^b	4 ^b	15 ^b
Copper roofs	0.8 ^g	2600 ^g	370 ^g	-	2600	-
Zinc roofs	1.0 ^g	153 ^g	6000 ^g	0.09	-	4000
Other impervious areas	0.8 ^g	23 ^g	585 ^g	0.150 ^d	4 ^d	15 ^d

^aexpressed as median value (minimum and maximum values are listed in brackets when available). ^bAhlman (2006). ^cLindgren (2001). ^dSum of dry and wet deposition. ^eExpressed as µg/kilometre driven. ^fModaresi et al. (2010). ^gGöbel et al. (2007)

Pollutant source data for European conditions (Table 4.2) are selected by using the same sources listed in the studies by Modaresi et al. (2010) and Ahlman (2006). Wide ranges are found in literature for some land uses (e.g. copper roof), with distributions where the median commonly differs from the mean of the interval.

The two SMC-based methods require the water volume to estimate pollutant loads. As flow measurements in the catchments covered only limited periods of time, a simple hydrological submodel (see the description in Section 5.2.2) is used to estimate the annual stormwater volume discharged from the catchments.

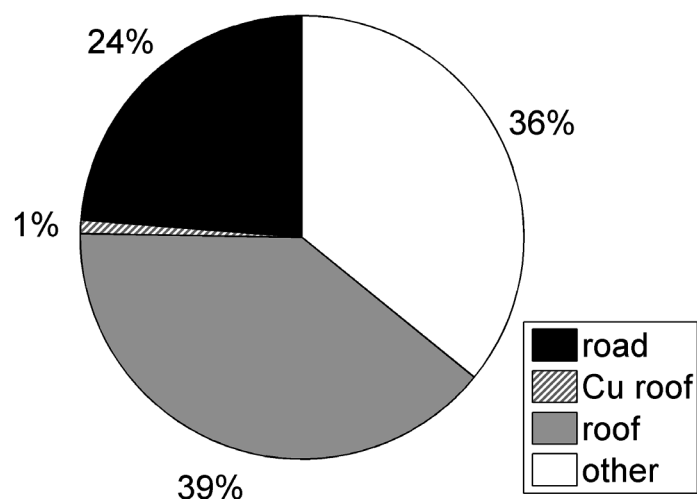


Figure 4.1. Distribution of land use in the Göteborg catchment.

The pollutant loads are estimated by using a simulated average runoff volume of $4.6 \cdot 10^4$ m³/yr for Göteborg (covering the period 2000-2010; see **Paper I**) and $2.58 \cdot 10^5$ m³/yr for Albertslund (period 1994-2004, see Section 7.3.2 and Appendix VI). The uncertainty of volume predictions is not considered here: the results uncertainty thus depends only on the ranges listed in Table 4.2.

4.3. Analysis of results

The heavy metal loads estimated by the three methods are shown in Figure 4.2 and compared with the loads calculated by using the measured SMC. The results uncertainty varies for different substances, with copper loads underestimated by all the three analyzed approaches. Measurements error is not considered in the analysis.

The lumped description of the catchment area (method A) provides good estimation of Cd loads (included within the estimated interval), but fails to provide good estimation of Cu and Zn loads. In both the studied catchments the SMC-based method combined with the detailed description of the catchment (method B) succeeds in bracketing the observed loads within the calculated interval for all the three metals. The release factor approach (method C) significantly underestimates the loads for all the metals, with an error ranging around 64-88% in Göteborg and 40-89% in Albertslund.

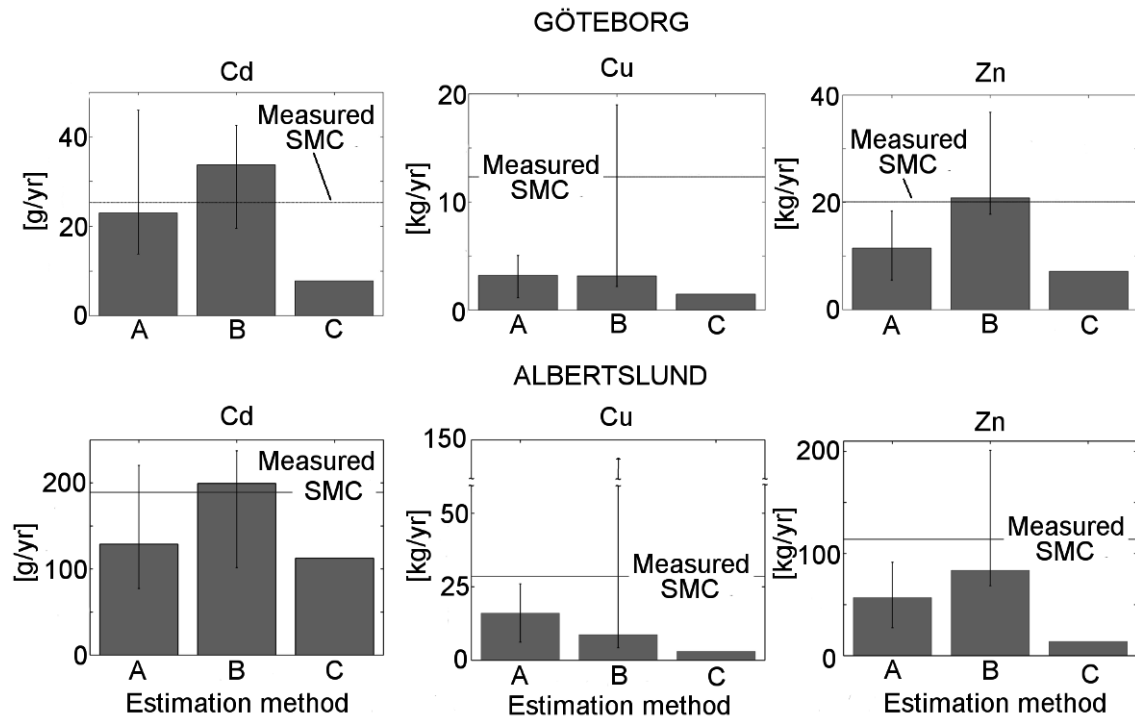


Figure 4.2. Comparison of the calculated heavy metal loads (Cd, Cu and Zn) discharged from the Vasastaden catchment in Göteborg for different estimation methods. The interval of estimated values is illustrated by the error bars.

The ability of the three methods of providing good estimation of stormwater loads clearly depends on the used dataset. Park et al (2009) demonstrated how the estimated loads varies by using different datasets, with significant uncertainty related to the spatial and temporal variability of stormwater pollutant sources (e.g. old datasets overestimate lead loads, as emission of this metal decreased due to its elimination from gasoline).

The use of different data from those listed in Table 4.2 (which may not fully represent the modelled catchments, as some of the data were collected outside Scandinavia and several years before the sampling campaigns in the study areas) may change the estimated loads. The possibility of identifying the major sources of uncertainty, i.e. the pollutant sources that require more attention, is an important feature for stormwater quality management. In fact, it allows the elaboration and evaluation of source control strategies, which is not possible with method A.

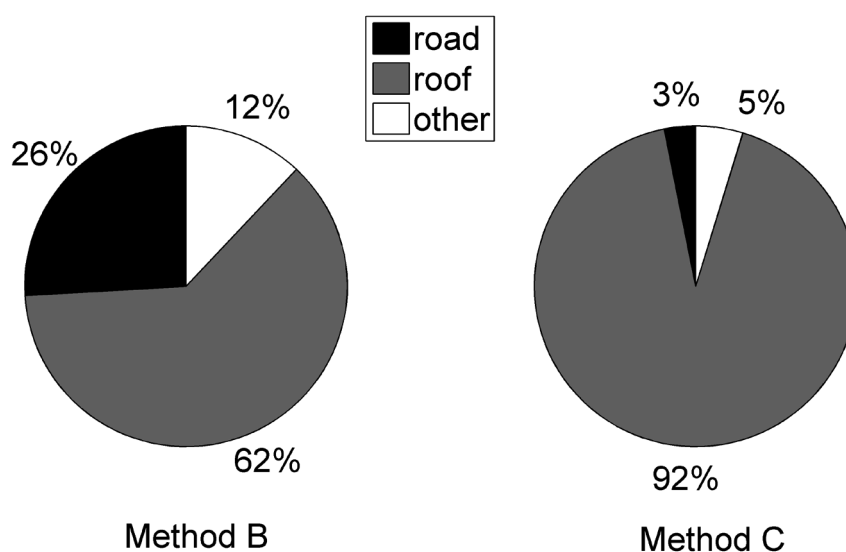


Figure 4.3. Distribution of Cu loads (mean values) for different areas (roads, roofs and other impervious areas) estimated for the methods employing a detailed catchment characterization.

The underestimation of Cu loads suggests that there are significant copper sources in the catchments that are not commonly present in the urban areas used to elaborate the values listed in Table 4.2. The lumped catchment characterization used in method A prevents the identification of such individual sources. Conversely, the detailed catchment characterization allows a substance flow analysis of the catchment and the consequent identification of the major copper sources. An example regarding the copper loads in the Göteborg catchment is presented in Figure 4.3.

Both method B and C pinpoint roofs as the major copper source in the Göteborg catchment. The ability of the SMC methods (A and B) to bracket the observation is mainly due to the wide Cu concentration range found in literature, ranging from 10 to 1000 $\mu\text{g/l}$. Furthermore, the two methods provide similar estimation of the Cu loads from copper roofs: 1.21 kg/yr for the SMC method and 1.27 kg/yr for the emission factor based method. A likely cause for this result may be (i) an underestimation of the Cu concentrations and release factors (i.e. the used dataset does not represent the situation in the Göteborg catchment), or (ii) erroneous classification of copper roofs and (iii) failure in the identification of all the potential Cu sources. To reduce the uncertainty in the Cu loads calculations can be necessary to focus the available resources on these two issues (estimation of release factors and identification of Cu sources).

This example shows that a lumped representation of the catchment (method A) does not allow the identification of the major pollutant sources and consequently cannot be used to assess potential pollution control strategies. Although requiring a lower amount of data and resources (time required to classify the area), this method decreases the possibility of modellers to improve their results. Conversely, a detailed catchment classification (method B and C) enables the modeller to identify the major sources of uncertainty in the estimation of PP loads and carefully consider them when modelling the release of stormwater pollutants. The latter approach is thus more suitable for assessing stormwater pollution control strategies.

5. Pollutant release and transport

5.1. Theoretical background

Modelling the release of stormwater pollutants from urban areas and across a drainage system is the core element of an integrated model for stormwater system. The model should account for the complex dynamic processes that affect the quality of the runoff collected and routed across the catchment. Since the first stormwater quality measurements in the 1970s, a great number of models have been developed (Tsihrintzis and Hamid, 1997; Elliot and Trowsdale, 2007; Obropta and Kardos, 2007). Different levels of complexity are used to model the two main output of the model: the water and pollutants fluxes (see Table 5.1). The hydrologic description of the system can adopt highly detailed, *mechanistic models* that are based on the theoretical description of the physical process (e.g. Saint Venants equations), or *conceptual models*, which reproduce hydrographs by representing the system as a combination of simple elements such as reservoirs. Conversely, stormwater quality models adopt lower level of complexity and may neglect the hydrological description by directly estimating pollutant loads (see Table 5.1).

The general difficulties in monitoring stormwater pollutants and in modelling the processes affecting their release and transport (Bertrand-Krawjewski, 2007) explain the lower level of complexity adopted in quality modelling compared to the hydrologic models. Three model typologies are used to model the pollutant concentrations and loads:

- *Conceptual dynamic models*: explain the processes taking place in the catchment with simplified formulations. The system is described through parameters that do not necessarily have a direct physical meaning, trying to represent the behaviour inferred from field observations (e.g. asymptotic accumulation of particulate pollutants on street surfaces).
- *Regression models*: these models estimate pollutant loads or concentrations based on regression of several parameters, which describe the pollutant sources and the characteristics of the catchment (e.g. traffic load) and the rainfall characteristics (volume, intensity, antecedent dry period). These models commonly provide event-based results.

- *Stochastic models*: these models express the pollutant concentration and loads as stochastic variables, so the results are expressed as probabilistic distributions. These models commonly provide event-based results.

The majority of the available dynamic models are conceptual models that try to represent the observed behaviour of particulate pollutants (such as TSS) on the catchment surfaces (e.g. roads, roofs). These models can thus be extended to the simulation of particulate PP or micropollutants with strong tendency to sorb (i.e. their fate is linked to the particles they are bound to).

The pattern of particulate pollutants on catchment surfaces can be schematized as follows (Figure 5.1): during dry weather pollutants accumulate on the surface resembling an asymptotic behaviour; during a rain event the pollutants are removed and washed off by runoff.

Table 5.1. Example of existing level of complexity for stormwater runoff quality models.

Level of complexity	Hydrologic model			Quality model		
	High		Low	Medium		Low
Example	Mechanistic	Conceptual	Neglected	Conceptual	Regression	Stochastic
Barbé et al. (1996)		X		X		
Behera et al. (2006)			X			X
Charbeneau and Barret (1998)			X		X	
Chen and Adams (2006; 2007)			X			X
FLUPOL (Bujon et al., 1992)		X		X		
HORUS (Zug et al., 1999a; 1999b)		X		X		
Kim et al. (2005)			X		X	
Opher and Friedler (2009)			X		X	
Osuch-Pajszinska and Zawilski (1998)		X		X		
Robien et al. (1997)			X		X	
Rossi et al. (2005)			X			X
SEWSIM (Ruan and Wiggers, 1997)		X		X		
SWMM (Rossman, 2009)	X			X		

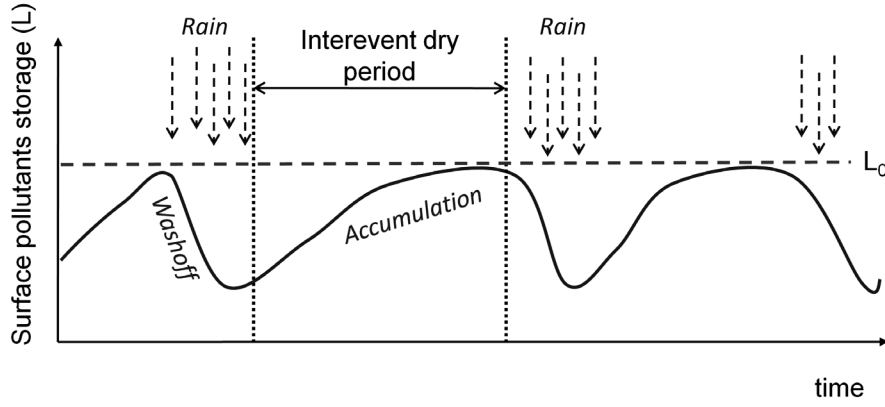


Figure 5.1. Behaviour of particulate pollutant loads on catchment surfaces (adapted from Vaze and Chiew (2002) and Behera et al. (2006)).

These two distinct processes have been described by several mathematical descriptions, which can be generalized by the following equation:

$$\frac{dL}{dt} = \theta_1 - \theta_2 L - \theta_3 R^n L \quad (5.1)$$

where L [M] is the mass of pollutant accumulated on the catchment surface. The first term of the equation assume a constant pollutant accumulation on the catchment that is expressed by the constant deposition rate θ_1 [M/T]. The second term assumes a “dry weather” removal, which is proportional to the available mass L and to the removal rate θ_2 [T⁻¹]. The latter accounts for the losses due to resuspension of particles (due to traffic, wind, etc.), degradation of the pollutant, and processes binding the particles (that are not available for washoff). The first two terms mathematically try to reproduce the asymptotic behaviour that is observed in real systems. This mathematical formulation has widely been applied in several models in the last decades (starting from Alley and Smith, 1981). Other formulations found in literature employ analytical solutions of Eq. 5.1 (e.g. Sartor et al., 1974; Grottke, 1987) or rewrite Eq. 5.1 to explicate the maximum mass of pollutant that can accumulate on the catchment (i.e. the asymptote L_0 in Figure 5.1 is equal to the ratio θ_1/θ_2) and to use it as calibration parameter. The formulations are mathematically equivalent, but they imply a different schematization of the modelled system and they depend on the available information. Eq. 5.1 uses the pollutant accumulation rate as parameter, which can be derived from source characterization: once the pollutant sources in the catchment are identified, emission rates (similar to those applied in source-flux-analysis and used in Section 4) can be estimated and applied in the model (e.g. Ahlman, 2006). The maximum load available on the surface represents the

equilibrium state in Eq. 5.1 and can be quantified by field measurements (Grottler, 1987; Vaze and Chiew, 2002). Conversely, the removal rate θ_2 can only be estimated indirectly. Other mathematical formulations (e.g. Charbeneau and Barret, 1998; Kim et al., 2006) are event-based and are thus less suitable for implementation in a continuous dynamic model.

The third term of Eq. 5.1 describes the washoff of pollutants from the catchment surface. Experimental data showed that the rainfall energy plays a role in the early stage of the rain event, whereas the available load of pollutant becomes important with the increasing duration of the event (Vaze and Chiew, 2003b). Pollutant washoff has been described by different mathematical formulations (e.g. Bertrand-Krajewski et al., 1993; Vaze and Chiew, 2003a), with various level of detail, ranging from the detailed physical model proposed by Shaw et al. (2006), to the spatial distribution of pollutants modelled by Deletic et al. (1997). Generally, these equations link the removal of particles to either rainfall intensity or to runoff, both expressed by the term R [L/T]. In the first case the model considers the raindrops' kinetic energy as the cause of pollutant removal and use the rainfall intensity (commonly one of the model inputs - e.g. Yuan et al., 2001) as forcing function. In the second case the removal of pollutants is caused by the stress caused by runoff flowing on the surface (Shaw et al., 2006) and R is expressed as runoff rate (runoff flow divided by the catchment area, commonly one of the model outputs - e.g. Alley, 1981).

The removal rate θ_3 [T^{n-1}/L^n] and the exponent n [-] are commonly considered as calibration parameters (Yuan et al., 2001; Vaze and Chiew, 2003a; Dotto et al., 2009; Kleidorfer et al., 2009; Avellaneda et al., 2009). The complexity of these formulations can be increased by adding additional parameters (e.g. Egodawatta et al., 2007), but all these equations can provide equally satisfactory results once the parameters are calibrated (Vaze and Chiew, 2003a).

As stormwater quality models have originally been developed for traditional pollutants such as TSS, the available models simulates the removal of particulate pollutants but do not represent other potential PP release process, such as corrosion or leaching from building materials (Clark et al., 2008; Schoknecht et al., 2009). These processes have complex dynamics, depending on the material and its use, rainfall characteristics, etc. (see for example the study on copper and zinc roofs in He et al., 2002). At the event time scale (hours), an initial peak in PP flux is observed, with a decrease to a constant value through time (Figure 5.2), which is independent from the rainfall intensity (Schoknecht et al., 2009).

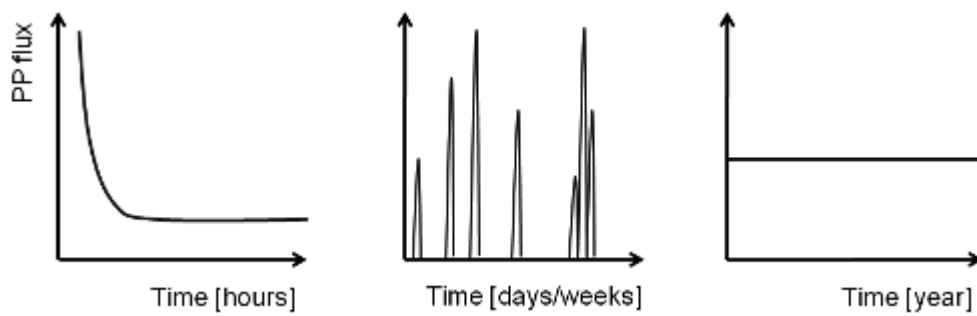


Figure 5.2. Schematic behaviour of release of soluble PP at different time scales (adapted from Odnevall Wallinder et al., 2004).

At bigger time scale, the discharged PP loads resemble those observed for particulate pollutants, with high inter-event variations that can be lumped into a constant value when looking at a long time scale.

Modelling of dissolved stormwater micropollutants is still relatively an unexplored area: few modelling examples are based on regression equations (e.g. Odnevall Wallinder et al., 2004; 2007) and conceptual models have been used in a risk assessment framework (Jungnickel et al., 2008; Burkhardt et al., 2009).

5.2. Developed approach

5.2.1. Research objectives

The previous section illustrates the wide choice of possibilities that are available for modelling stormwater quality. The modeller can choose between different levels of complexity for water and pollutant simulation (Table 5.1), selecting different approaches to model the complex dynamic processes that drive release and transport of PP. A trustworthy application of these models requires the investigation of the performance of these models and the quantification of the result uncertainty.

The research presented in this part of the thesis thus aims to investigate how existing statistical methods can be used to (i) achieve a better knowledge of stormwater quality models and (ii) estimate the model result uncertainty. These results would enable a wider application of these models for practical purpose. This research starts from conceptual stormwater quality models, which represent a compromise between the maximum level of complexity in stormwater quality modelling and the resources (computational and modeller's time) needed for running the simulation.

The results can also be compared with the outcomes presented by several authors that assessed the uncertainty of stormwater quality models with similar level of complexity for traditional macropollutants (e.g. Gaume et al., 1998; Kanso et al., 2005; 2006; Dotto et al., 2009; Kleidorfer et al., 2009) and micropollutants (Lindblom et al., 2007b,submitted)

5.2.2. Model description

The stormwater quality model used in this thesis is based on the accumulation-washoff model initially proposed by Alley and Smith (1981) and subsequently applied in several models, such as the SEWSYS model (Ahlman, 2006) that was used as starting point to simulate pollutant fluxes. The model implemented and used in this thesis runs in the MATLAB/SIMULINK environment with continuous time, differing from the discrete time step approach adopted in SEWSYS (a similar continuous time model is used by Lindblom et al., 2007a; 2007b).

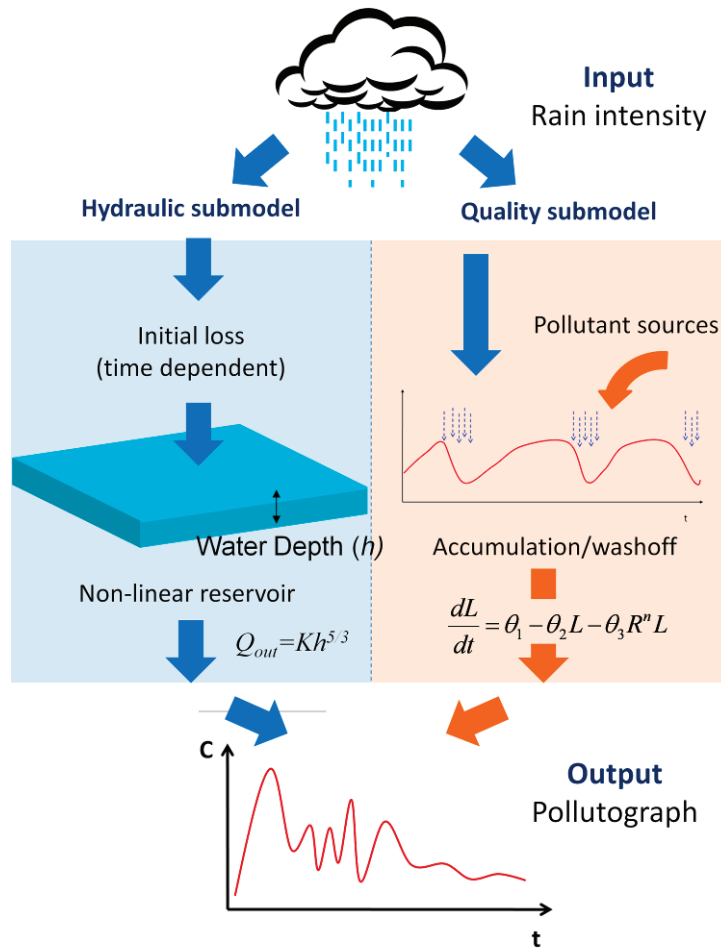


Figure 5.3. Sketch of the conceptual stormwater quality model used in **Paper I**.

This conceptual model considers several pollutant sources present in the urban environment (e.g. dry and wet deposition, traffic, building material corrosion, etc.). The use of continuous time steps allows for the implementation of a novel loss model (which neglects the “antecedent dry period” as model parameter and introduces a time interval required by the catchment to return to dry conditions), as well as an improvement in the simulation speed compared to discrete time models. The model is subdivided into two submodels (Figure 5.3): hydrologic (estimating the flow discharged from the catchment) and quality (calculating the pollutant mass fluxes).

The hydrologic submodel estimates the outlet hydrograph by using the non-linear reservoir approach. The catchment is represented as a reservoir with area equivalent to the catchment reduced area A [m²]. The water balance of the reservoir is described by the following equation:

$$\frac{dW}{dt} = Q_{in} - Q_{out} \quad (5.2)$$

where W [m³] is the volume of runoff stored in the reservoir; Q_{in} [m³/s] is the inflow to the reservoir and Q_{out} [m³/s] is the catchment outflow. The first term is calculated by considering the hydrological reduction factors K_{run} [-] and R [m/s], which is the effective rainfall intensity. This is equivalent to the rainfall input after that the initial loss threshold (defined by h_{Dunne} [m]) is exceeded:

$$\begin{aligned} Q_{in} &= 0 && \text{for } R \neq 0 \text{ and } h_{cum} \leq h_{Dunne} \\ Q_{in} &= K_{run} \cdot A \cdot R && \text{if } R \neq 0 \text{ and } h_{cum} > h_{Dunne} \end{aligned} \quad (5.3)$$

where h_{cum} [m] is the cumulated rainfall height from the beginning of the rain event. The initial loss accounts for the wetting processes that take place in the catchment before runoff is observed. After the end of rainfall events, the model simulates the drying processes by linearly decreasing h_{cum} , which returns to zero after a time T_{Dunne} [s] (i.e. the catchment is back to dry conditions).

The outflow from the catchment (Q_{out}) is calculated as:

$$Q_{out} = K_m \cdot h^{5/3} \quad (5.4)$$

where the routing parameter K_m [m^{3/5}s⁻¹] expresses the physical characteristics of the catchment and affects the shape of the outlet hydrograph and h [m] is the fictitious water level in the catchment (calculated as the ratio between W and A).

The quality submodel simulates the accumulation-washoff of pollutants based on Eq. 5.1. The pollutant deposition rate θ_I is calculated according to the stormwater pollutant sources in the catchment (copper and zinc roofs, traffic loads, etc.), while the contribution of wet deposition is modelled as a flux entering the catchment during rain events.

The outputs of the hydrological submodel is the outlet flow M_{flow} [m³/s] (i.e. the outlet from the non-linear reservoir), while the output from the quality submodel is the mass flux M_{Mass} [g/s] (i.e. the third term in Eq. 5.1). By combining these two outputs it is possible to calculate the outlet concentration M_{Conc} [g/m³].

5.3. Analysis of model performance

The model described in the previous paragraph has two submodels with specific parameters and two inputs (rainfall and wet deposition fluxes, which can be affected by error), for a total of nine model factors (Table 5.2) that can contribute to the model results uncertainty. To include the uncertainty on the estimation of pollutant source releases (i.e. the factors used for method C in Section 4), the release factor θ_I is here treated as a model parameter. When dealing with such complex models it is necessary to gather a good knowledge of the model behaviour, which allows focusing the available resources on the most sensitive factors to estimate the model uncertainty bounds.

Regarding the interactions between model parameters, previous studies (Kanso et al., 2006; Lindblom et al., 2007a; Dotto et al., 2009) showed correlations between the parameters of the quality submodel. The application of GSA and pseudo-Bayesian methods is thus straightforward, as these techniques are capable of identifying the relationships between parameters (GSA) and do not require a prior definition of the parameter correlation structure (GLUE). Also, the hydrologic submodel can affect the concentration calculations and it might compensate for the uncertainty of the accumulation-washoff parameters. Generally, this aspect is neglected and the performances of the two sub-models are assessed independently, with the quality submodel run by using observed flows or the flow generated by the calibrated hydrological submodel (e.g. Lindblom et al., 2007a; Dotto et al., 2009; Kleidorfer et al., 2009).

The examples presented in this thesis investigate the application of GSA in two case studies. The model is applied to two catchments with similar size (4.8 ha and 2.2 ha, respectively) located in Göteborg (Sweden – see the description in **Paper I**) and Oslo (Norway - see description in Vollertsen et al., 2007).

Table 5.2. List of model factors (inputs and parameters) for the stormwater quality model (from **Paper I**)

Factor name	Unit		Description
K_m	$m^{3/5}s^{-1}$	Hydrologic submodel parameter	Routing coefficient related to catchment characteristics
K_{run}	-		Hydrological reduction factor
h_{Dunne}	m		Initial loss
T_{Dunne}	hr		Time required to dry the catchment
θ_1	$\mu g/m^2/s$	Quality submodel parameter	Pollutant deposition rate
θ_2	s^{-1}		Dry weather pollutants removal rate
θ_3	mm^{-1}		Rain pollutant removal rate
err rain	-	Model inputs	Error on rainfall intensity
wet dep	-		Error on rain pollutants concentration

The sampling techniques of these two datasets are representative of the stormwater quality data that are available in literature: while the Göteborg data provide detailed information for a short sampling period (57 samples for 13 rain events over two months), the Oslo data give a longer overview of the system (20 samples for 65 rain events, covering a six-month period). Although several stormwater micropollutants were measured in the mentioned case studies and can be simulated by the model, this study focused only on copper to facilitate the comparison of the results with previous studies (Lindblom et al., 2007a; 2007b).

5.3.1. Identification of important model factors

The important model factors are identified by applying the Variance Decomposition Method described in Section 3.4.1. The results from **Paper I** stress the high computational requirement needed by this method, as a total of 190,000 model runs are required to obtain a complete overview of the interactions between parameters. Nevertheless, the GSA results provide a deep insight in the model behaviour, which cannot be achieved by using traditional OAT methods. The Sensitivity Index (S_I) and Total Sensitivity Index (S_{Ti}) are calculated for likelihood responses calculated for two different outputs of the quality submodel (M_{mass} and M_{conc}), but no major differences is noticed between the two outputs (Figure 5.4).

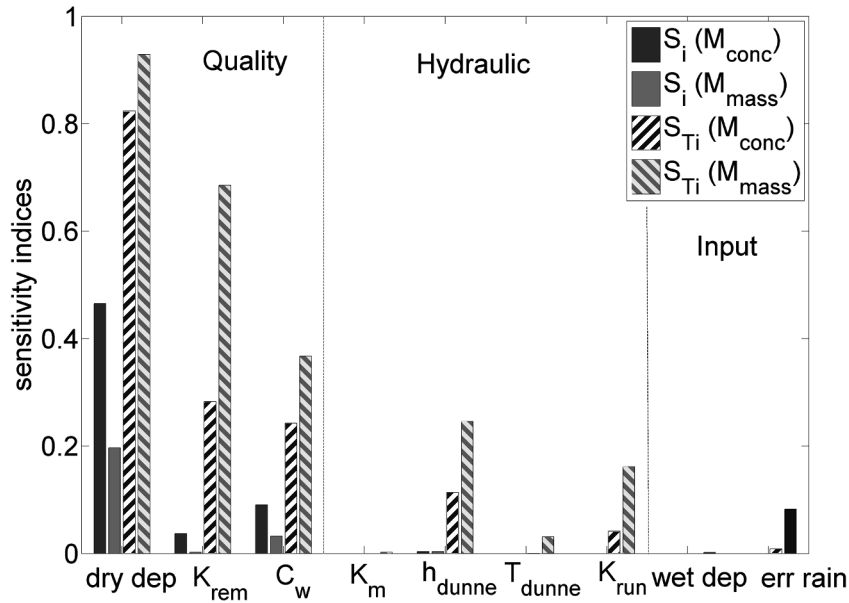


Figure 5.4. First order (S_i) and total (S_{Ti}) sensitivity indices estimated for the likelihood on concentration (M_{Conc}) and mass (M_{Mass}).

Both the sensitivity indices for the mass and the concentration highlight strong interactions between the quality submodel parameters, confirming the correlation found for TSS by Kanso et al. (2006) and Dotto et al. (2010), and for Cu by Lindblom et al. (2007a). A traditional OAT method, or a sensitivity analysis based only on the analysis of the S_i would neglect the influence of the hydrologic submodel on the output.

The Total Sensitivity indices, however, show that the parameters driving the water volume (initial loss h_{dunne} and the hydrological reduction coefficient K_{run} and – at a lower level – the error on the rainfall input *err rain*) interact with other parameters and thus affect the variance of the model output.

The influence of the hydrologic parameters (responsible for up 30-40% of the output variance in some phases of the rain event) can be visualized by looking at the sensitivity indices calculated at each simulation time step (Figure 5.5): while the initial loss importance is high during the initial phase of the rain event, the runoff coefficient increases its relevance during the rain event, i.e. when the majority of the pollutant mass has been removed and the discharged loads (and concentrations) mainly depend on the water volume.

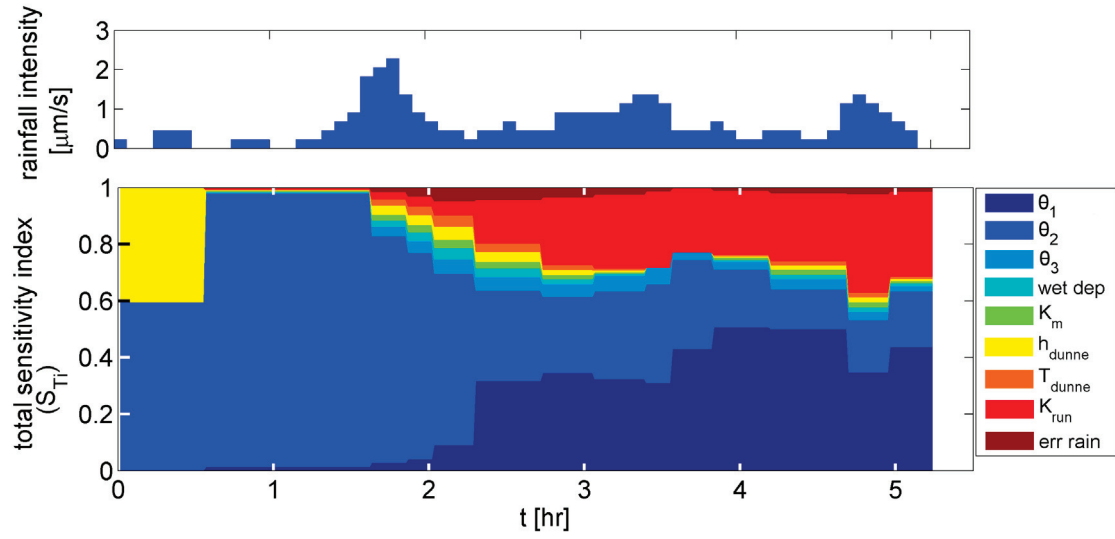


Figure 5.5. Temporal behaviour of the normalized total sensitivity index (S_{Ti}) for M_{Conc} for a rain event recorded in Göteborg (from **Paper I**).

These results show how a comprehensive GSA method can fully investigate the behaviour of a dynamic model and provide a detailed description of the significance of the model factors and their interactions. This information is relevant to identify the major sources of model uncertainty, to focus the available resources on the significant factors and to quantify (and potentially reduce) the model prediction bounds.

5.3.2. Uncertainty analysis

The GSA results provide the basis for the uncertainty analysis and the subsequent quantification of the model result uncertainty: non-sensitive factors are in fact disregarded, while the large number of simulations generated in the GSA can be recycled to estimate the model prediction bounds. Starting from the results presented in the previous section, GLUE is applied on the five most sensitive (θ_1 , θ_2 , θ_3 , h_{Dunne} , K_{run}) parameters and model performance is evaluated for four different likelihood measures (see section 3.4.2 and **Paper I**) and two model outputs (M_{Mass} and M_{Conc}).

The GLUE analysis generates outputs that can be presented in various ways, offering an overview about the model characteristics and its ability to represent the observed values. The behavioural parameter sets can be presented in cross-correlation plots (as the one showed in Figure 5.6). The analysis of this graph enables the identification of interactions between model factors, such as the relationship between θ_1 and θ_2 . This result confirms the GSA findings, which

identified a relationship between those two parameters defining the mass of pollutant accumulated on the catchment surface.

Some relationships, such as the one between the runoff coefficient K_{run} and the deposition rate θ_1 depends on the model output that is used to calculate the informal likelihood (in this example M_{conc}), as shown in Figure 5.7. These relationships are explained by the model's structure: as θ_1 and θ_2 define the total mass that can be accumulated on the surface (as explained in Section 5.1), the correlation with K_{run} is caused by the calculations used to estimate the concentration M_{conc} (in fact, such relationship is not seen when estimating the likelihood for M_{Mass}).

These illustrated interactions between parameters stress the benefits deriving from the application of GLUE, which does not require *a priori* definition of the parameter correlation structure. In fact, this feature avoids the need for a model re-formulation, as conversely Bayesian methods would require (see the case described in Kanso et al., 2006).

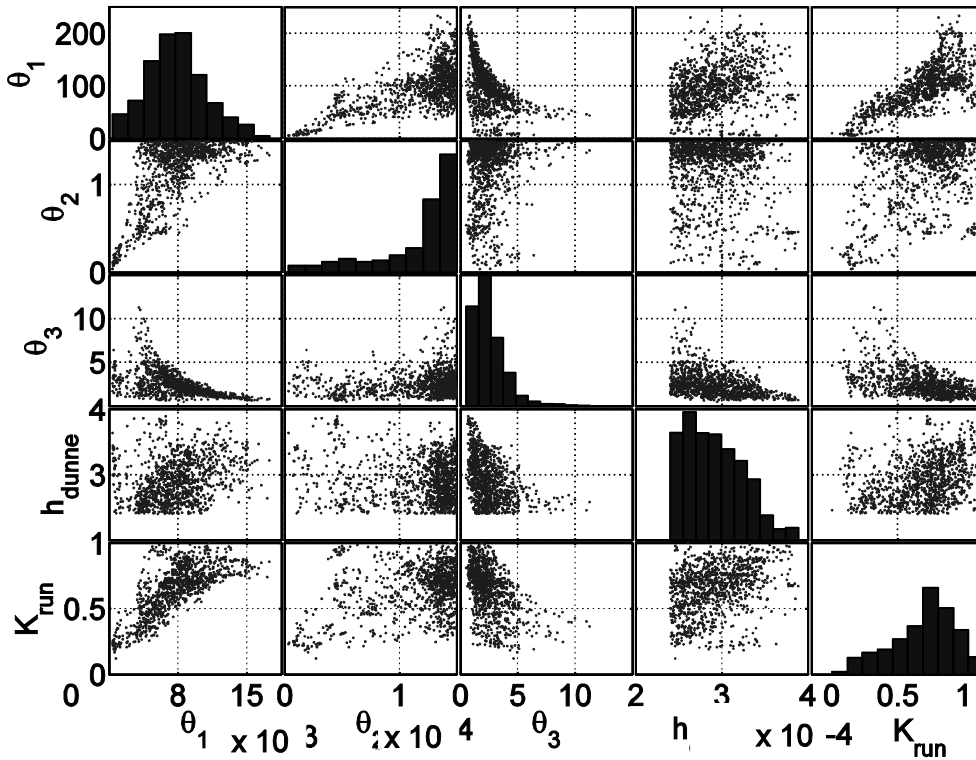


Figure 5.6. Cross correlation plot of the behavioural parameters identified by using the Nash-Sutcliffe likelihood for Cu concentration.

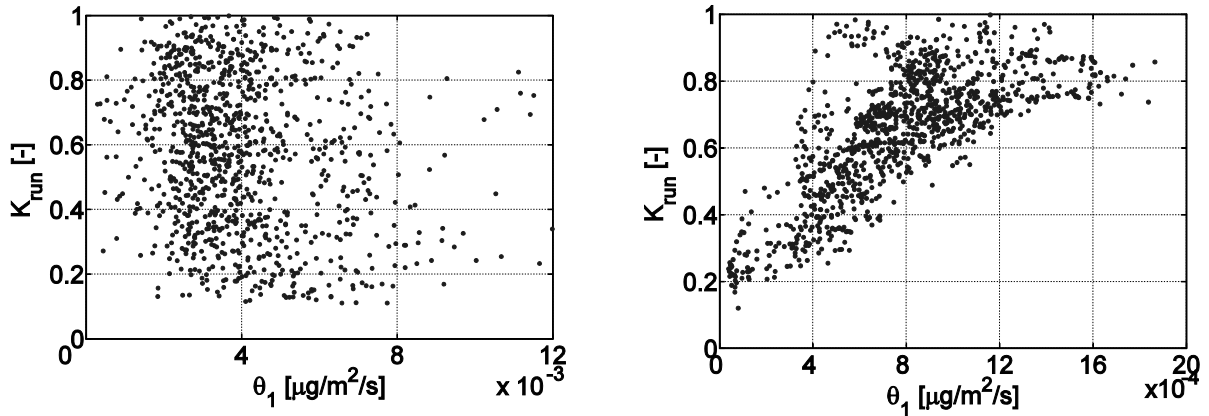


Figure 5.7. Cross correlation plots between the pollutant deposition parameter θ_1 and the runoff coefficient K_{run} for M_{Mass} (on the left) and M_{Conc} (on the right).

The model performance analysis highlights the difficulties that stormwater quality models encounter in simulating the initial and the final phase of a rain event, i.e. the initial concentration peak and the final descending phase of the pollutograph (confirming the results obtained by, among others, Haiping and Yamada, 1998; and Avellaneda et al., 2009). These limitations can be compensated by the likelihood measure that is used to estimate the model prediction bounds: the Nash-based likelihood, for example, tends to focus on the average behaviour of the entire dataset and to treat the initial concentration peaks in the pollutograph as outliers.

This phenomenon can be visualized by comparing the prediction bound for the pollutographs simulated in the Göteborg catchment and estimated by using different likelihood measures: Figure 5.8 shows the bounds estimated with the variance-based likelihood (Eq. 3.9 - above) and with the Nash-Sutcliffe based likelihood (Eq. 3.10 - below). Both prediction bounds are created by using the same acceptance criterion for behavioural models (91.2% of the observed values within the bounds).

The Nash-Sutcliffe based likelihood bounds fails to cover the concentration peaks in the beginning of rain events (e.g. the samples identified by I and IV in the pictures), while the variance based likelihood includes those samples within the model prediction bounds (and this leads to wider prediction bounds). The variance based likelihood measure, in fact, tends to minimize the simulation error for all the samples without distinctions between samples that lie around the average value and those that present bigger deviation.

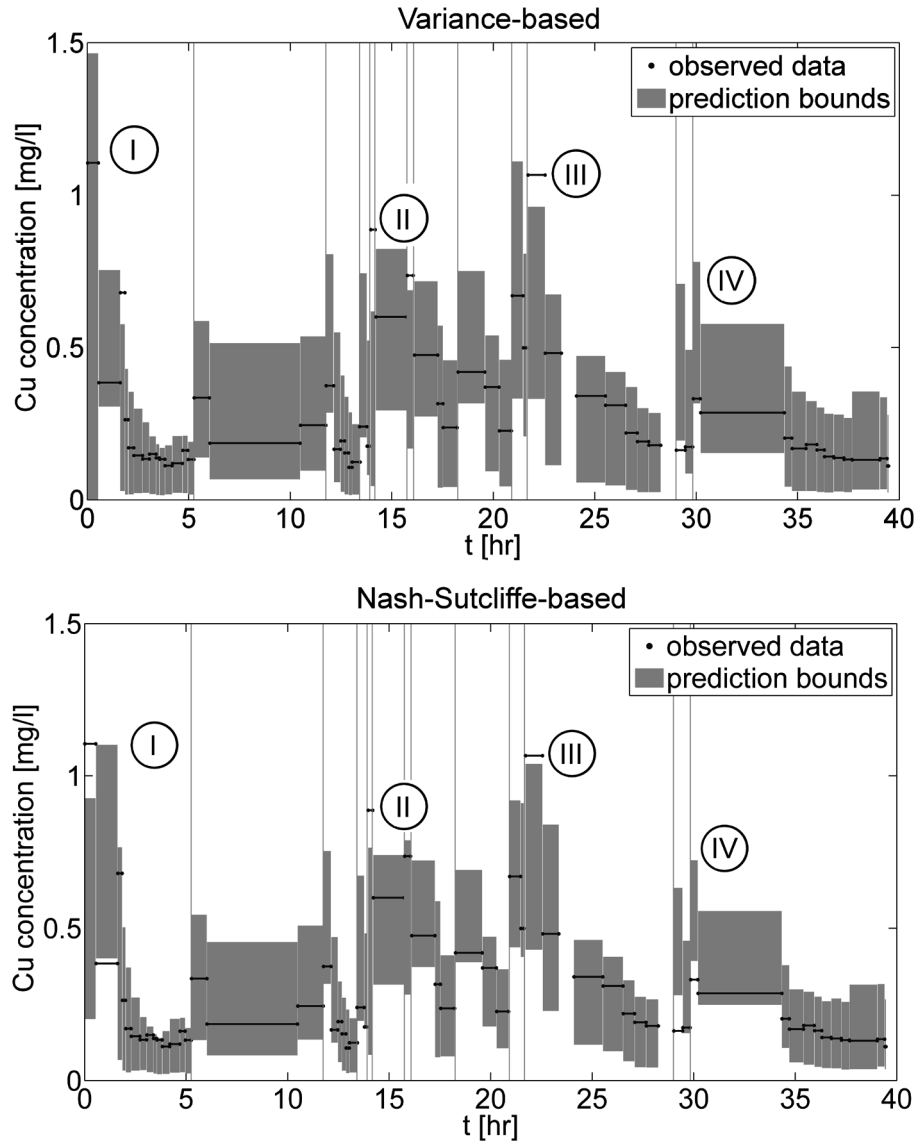


Figure 5.8. Prediction bounds for Cu concentration in Göteborg estimated by using variance-based likelihood (Eq. 3.9 – above) and Nash-Sutcliffe based likelihood (Eq. 3.10 - below) on M_{Conc} (13 rain events).

The variance-based likelihood thus looks more appropriate for the particular shape of pollutographs prediction bound, conversely to the Nash-Sutcliffe likelihood, which is more appropriate for outputs with great number of data and smoother patterns (e.g. flow data, for which the Nash-Sutcliffe criterion was originally developed). The choice of an appropriate likelihood measure does not hide the model structural deficiencies: regardless of the chosen likelihood measure, the model failed to simulate some events (identified by II and III in Figure 5.8).

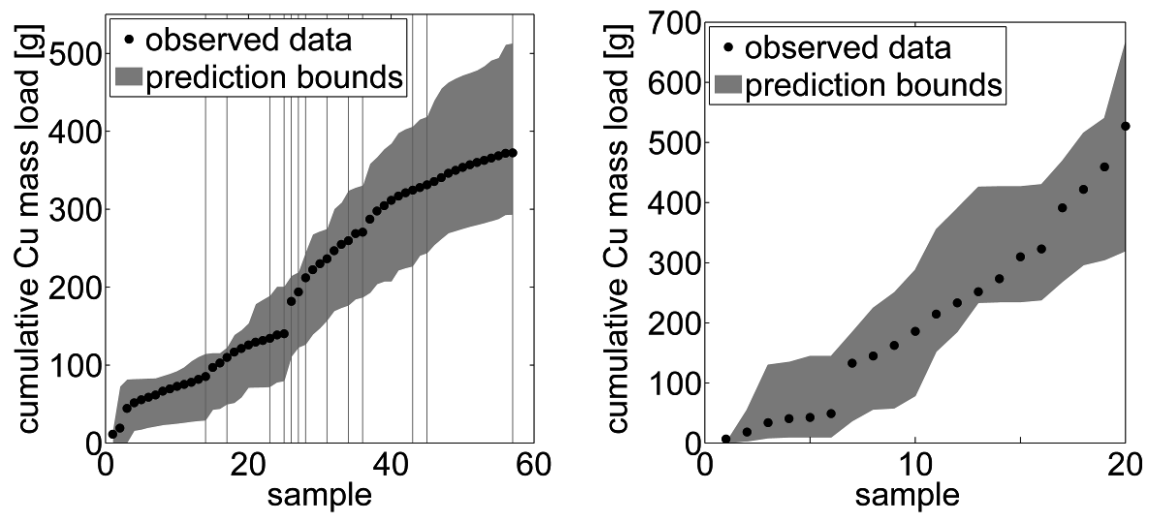


Figure 5.9. Prediction bounds for Cu cumulative loads for Göteborg (on the left) and Oslo (on the right). Bounds are estimated by using the variance-based likelihood.

Generally, the model shows better performances when looking at the cumulative loads discharged from the catchment: the average width of the prediction bounds for mass are about half of the width for concentration (see **Paper I** for further details). The uncertainty of the results are less affected by the choice of the likelihood or by the sampling technique used to obtain the measured data. Figure 5.9 shows a comparison between the cumulative Cu loads estimated for Göteborg (where the 57 samples were collected during 13 rain events, with several inter-event samples) and for Oslo (where several rain events were lumped in 20 composite samples).

Despite the different characteristics of the catchments, the number of available data and the different sampling techniques, the results shows comparable uncertainty: $+38\%/-21\%$ for the mass discharged from Göteborg (during a 2 months period) and $+26\%/-39\%$ for Oslo (during a 6 months period). The magnitude of this error is comparable with the one estimated for measurement-based load calculations (estimated around 30-40% by Bertrand-Krajewski and Bardin, 2002). The width of the prediction bounds for Cu mass in Göteborg (293-513 g) is smaller than the bounds estimated by Lindblom et al. (2007a), which ranged in between 209-576 g. The smaller bounds obtained in this thesis are originated by the inclusion of the hydrologic submodel in the uncertainty analysis and by the use of a different likelihood measure. These outcomes show how the application of uncertainty analysis techniques allows the quantification of uncertainty for stormwater quality models, providing a basis for a practical application of these models.

5.3.3. Uncertainty in model application

To demonstrate how the results from the uncertainty analysis can be used for practical purposes, the model is applied to perform long-term simulations for the Göteborg catchment. The model generates three outputs that can be used to evaluate the situation in the study area (Figure 5.10):

- A1. The pollutant loads discharged from the catchment (to assess the long term impact of stormwater on the receiving waters).
- A2. The frequency of exceedance of Emission Limit Values for copper (to assess the potential acute impact of stormwater on the water environment)
- B1. The potential frequency of overflow of a stormwater treatment unit to be placed at the catchment outlet (to assess the efficiency of strategies for reducing stormwater pollutants emissions). For this scenario the maximum flow capacity conveyed to the BMP is set to 250 l/s.

To ensure that both flow and concentration predictions are realistic, the model is run by using the behavioural parameters selected with a combined likelihood measure including flow and concentration (M_{flow} and M_{conc} - see **Paper I**). This also ensures good prediction of pollutant loads.

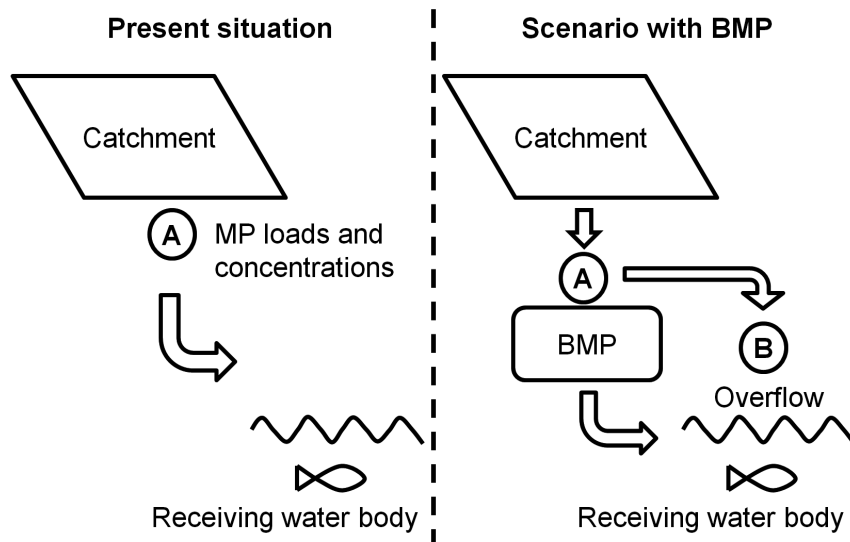


Figure 5.10. Scheme representing the different model outputs (from **Paper I**).

Table 5.3. Results from 10-year simulations for the Göteborg catchment (these results integrate those presented in Paper I).

Model output		Mean value	Prediction bounds (min and max)
Average runoff volume [m ³ /yr]		4.61·10 ⁴	2.74·10 ⁴ – 5.84·10 ⁴
A1	Total pollutant discharge [kgCu/yr]	11.1	5.54 – 18.4
A2	Fraction of discharges exceeding of Cu quality criterion ^a [%]	96.5 ^b	93.0 – 99.8 ^b
B1	BMP overflow events [yr ⁻¹]	5.38	1.10 – 9.00
B2	Loads discharged by overflows [gCu/yr]	409	15.7 – 322
B3	Fraction of overflows exceeding Cu quality criterion ^a [%]	69.9 ^b	45.0 ^b – 100 ^b

^a set to 12 µg/l for dissolved phase, according to Danish regulation (Danish Ministry of Environment, 2006).^b Dissolved phase estimated with k_d equal to 52500 l/kg (mean value from Shafer et al. (2004)) and TSS concentration of 228 mg/l (Ahlman, 2006).

A 10-year rainfall series recorded in the period 2000-2010 is used as model input, and the simulation results are listed in Table 5.3. The table provides the final user with a mean value, which conveys the information about the simulated system, and with prediction bounds, which express the reliability of the model outcomes.

The difference from the Cu load calculated by using the measured Site Mean Concentration (see Section 4.3) is lower than 10% (11.1 kg/yr for the dynamic model and 12.3 kg/yr for the static model, see Figure 4.2). As quality standards are commonly fixed only for the dissolved phase, the concentration of the Cu phases is calculated from the simulated total Cu value by using the water-soil partition coefficient k_d (following the same assumptions made in the development of the treatment model – see Section 6.2.2 and **Paper II**).

The estimated Cu loads vary in a -50/+60 % range from the median value. The model suggests that stormwater discharge from the study area may cause acute impacts on the receiving waters. In fact, the EMC for the majority of the rain events (over 92%) exceeds the ELV for dissolved copper. The model also shows that the installation of a BMP with a capacity of 250 l/s would intercept the majority of the copper loads. The loads discharged by flows bypassing the BMP, in fact, are generally below 2-3% of the total annual loads. The installation of a BMP would also reduce the acute impacts on the receiving body, as the fraction of discharges exceeding ELV for dissolved copper are reduced.

These results provide an understanding of the impact of stormwater pollution in the catchment. The listed uncertainty bounds convey information regarding the reliability of these results, providing the basis for a wider (and more reliable) application of dynamic models in stormwater pollution management. The combination of this model with stormwater treatment models (as the one presented in Section 6.2.2) would allow the complete evaluation of different pollution control strategies (see Section 7.3.2).

6. Treatment

6.1. Theoretical background

The existing software for stormwater quality simulation offers several options for modelling stormwater treatment units (see for example the review in Huber et al., 2006). Compared to e.g. the IWA ASM models for wastewater treatment (Henze et al., 2000) or the RWMQ for river systems (Reichert et al., 2001), these models commonly present a low level of process complexity. The level of uncertainties affecting stormwater quality modelling is significant, and this leads modellers to commonly prefer highly lumped and conceptual models.

The existing models (a brief list is presented in Table 6.1) can be classified according to several criteria and attributes (e.g. pollutants simulated, removal processes, model purpose, time steps, etc.). These models usually include “traditional” water quality pollutants and heavy metals. The latter, however, are commonly only related to suspended solids and their settling process through e.g. regression relationships, and other fate processes (e.g. adsorption, chemical transformation, bioaccumulation, etc.) are not included (see for example Walker and Hurl, 2002). The existing models do not allow the simulation of the fate of heavy metals without field data used to calibrate regression relationships, nor to simulate the fate of organic PPs with more complex behaviour and removal processes (such as hydrolysis, photolysis, and biodegradation).

The lack of modelling tools capable of simulating the removal of Priority Pollutants in stormwater treatment units is partly caused by the novelty of the problem. Only in the last decade, in fact, Priority Pollutants from stormwater discharge has been recognised to pose an environmental risk (Eriksson et al., 2007; Kayhanian et al., 2008; McQueen et al., 2010). The major challenge impeding the development of models in this area is however the general lack of PP measurements in stormwater treatment units. Data are available for some specific units (e.g. DiBlasi et al., 2009; Hatt et al., 2009a; 2009b), and existing databases (e.g. Wright Water Engineers, 2007) allow the application of simple removal efficiency-based models (e.g. Ackerman and Stein, 2008).

Table 6.1. Models for simulation of urban BMP performances (adapted from Huber et al., 2006; and Elliot and Trowsdale, 2007).

Model	Reference	Acronym	Removal process	MP	Ponds	Infiltration Trenches	Grass Swales	Extended Detention	Bioretention and wetlands	Filter Strips	Porous Pavement
Dynamic Model for Stormwater Treatment Areas	Walker and Kadlec (2008)	DMSTA	Settling		X				X		
Model for Urban Stormwater Improvement Conceptualisation	MUSIC development team (2005)	MUSIC	Lumped first order	(X)	X	X	X	X	X	X	(X)
Program for Predicting Polluting Particle Passage through Pits, Puddles and Ponds	Walker (1990)	P8	Removal efficiency	(X)	X		X		X	X	
Pollutant Removal Estimates for Wetland design	Dortch and Gerald (1995)	PREWET	Lumped first order	X					X		
RUNoff QUALity from development sites	Haith (1999)	RUNQUAL	Removal efficiency	(X)	X	X			X	X	
Source Loading and Management Model	Pitt et al. (1999) Pitt and Voorhees (2002)	SLAMM	Settling (pond and wetlands) or removal efficiency (the remaining units)	(X)	X	X	X			X	X
StormTac	Larm (2003)	StormTac	Settling		X		X		X		

Model	Reference	Acronym	Removal process	MP	Ponds	Infiltration Trenches	Grass Swales	Extended Detention	Bioretention and wetlands	Filter Strips	Porous Pavement
Stormwater Management Model	Rossmann (2009)	SWMM	Removal efficiency		X	(X)	X	(X)	X	(X)	(X)
Virginia Field Scale Wetland Model	Yu et al. (1998)	VAFSWM	Settling and adsorption						X		
Urban Volume and Quality	Mitchell and Diaper (2005)	UVQ	Removal efficiency	(X)	X	X			X		
Wetland water balance and nutrient dynamics model	Lee et al. (2002)	WETLAND	Monod kinetics						X		
Watershed Management Model	Wayne County (1998)	WMM	Removal efficiency	X (only metals)	X		X	X			
X	modelled	(X)	not explicitly addressed, but could be modelled indirectly								

Based on the formulation of the removal processes, the available models can be divided into different classes (see also Table 6.1):

- *Removal efficiency based models*: a detailed description of the removal processes and kinetics is neglected. The water quality improvement is simply estimated by using a reduction factor, which can be retrieved from available databases (Wright Water Engineers, 2007) or calculated by using empirical equations (like in SWMM). P8 and WMM, for example, apply this approach.
- *First order kinetics based models*: the pollutant removal is modelled by a single first-order reaction, which lumps into a single coefficient all the different processes taking place in the treatment unit. This approach has been applied in MUSIC and PREWET.
- *Settling based models*: settling of particles is considered as the main removal process. The removal of other pollutants is calculated by assuming sorption of the substance to the settled particles through partition coefficients. An example of this approach can be found in DMSTA (combined with a multi-CSTR approach) or in the wetland modelling applied in SLAMM. The VAFSWM model couples settling processes with adsorption of pollutants to particles. Mechanistic models based on settling processes are presented for example in Bentzen (2008) and Pathapati and Sansalone (2009).
- *Pollutant cycle based models*: the cycle of the different pollutants are modelled by considering the transformations occurring in the unit (e.g. bacterial and vegetation growth, sorption, etc.). This formulation is characterized by a higher complexity level than the other models. These models are usually applied for nutrients in wetlands, where the quality of available information is sufficient to allow such complex models and realistic description of the system (e.g. Lee et al., 2002)

Each model can be used to simulate a different number of BMP, with SWMM and MUSIC that can simulate the greater number of treatment facilities (Table 6.1). The latter is characterized by a flexible approach, based on serial Continuously Stirred Tank Reactors (CSTR), which allows the simulation of facilities with different hydraulic behaviour.

The number of CSTR tanks (N) is in fact defined to reproduce the behaviour of the desired stormwater treatment unit (with an infinite number of tanks equal to a plug-flow reactor). This approach is widely applied in environmental modelling (e.g. Werner and Kadlec, 2000; Kadlec, 2000) and relies on several studies for the definition of the model parameters (e.g. the number of tanks N needed to simulate the system— see for example by Jansons et al., 2005). This feature reduces the need for field measurements for the calibration of the hydraulic parameters.

The hydraulic performances of stormwater units and the deviations from the design flow conditions can be summarized by the hydraulic efficiency value λ (Persson et al., 1999):

$$\lambda = e_v \left(1 - \frac{1}{N} \right) = \frac{\tau_p}{\tau_n} \quad (6.1)$$

where e_v [-] is the effective volume ratio (defined by the proportion of storage volume in the unit that is actively participating in the flow through the unit), τ_p [T] is the peak of the hydraulic residence time distribution in the real system (i.e. the time when the highest tracer concentration is passing through the outlet after a tracer impulse is emitted in the inlet) and τ_n [T] is the nominal residence time in the unit (usually the design criterion). In models based on serial tanks, like MUSIC, the number N of CSTR is defined to obtain values of λ that are similar to those recorded (or simulated with detailed hydrodynamic models, e.g. Jansons et al., 2005) in BMP with comparable layout.

6.2. Developed approach

6.2.1. Research objectives

A flexible approach for estimating the fate (and thus the removal) of stormwater pollutants in a wide range of stormwater treatment units has been proposed by Scholes et al. (2008a) and Revitt et al. (2008), and subsequently extended to Priority Pollutants in Scholes et al. (2008b). This method combines an assessment of the potential fate processes taking place in stormwater units with the tendency to be affected by different fate processes of a given substance, based on its inherent properties. The method provides only a preference ranking of the BMPs for removing a specific substance (or a family of substances).

However, the assessment of PP reduction strategies might also require quantitative information, i.e. data showing the expected PP emission reduction provided by a specific BMP (or combination of BMP).

The results presented in this thesis illustrate the features of the Stormwater Treatment Unit model for MicroPollutants (STUMP - **Paper II**), where the term MicroPollutants (MP) is used as synonym for PP to avoid misunderstanding with the ASM terminology (where PP refers to polyphosphate - Corominas et al., 2010). This model includes different fate processes that need to be accounted for simulating the fate (and removal) of a wide range of MP in stormwater treatment systems. STUMP is also built to model different stormwater treatment units under dynamic conditions, merging this characteristic with features that are common to large-scale multimedia models (such as the fate modelling based on the substance inherent properties). The model is developed based on three main criteria which aimed to:

- Utilize all the available information on pollutants: given the general lack of field measurements, substance's inherent properties can provide important information about the fate of a micropollutant. The equations used to model MP fate processes in STUMP are thus based on the substance's inherent properties, with an approach similar to the one adopted in environmental chemical risk assessment (e.g. European Communities, 2003). This approach also enables the integration of STUMP with other models developed based on the same principle (e.g. sewer network, WWTP, receiving water - see for example Benedetti et al., 2009), allowing the simulation of integrated urban wastewater systems and their interactions with the surrounding environmental compartments (atmosphere and groundwater - see the example presented in De Keyser et al., 2010).
- Benefit of existing knowledge: a wide range of modelling tools is already available to simulate “traditional” macro-pollutants (Table 6.1). The project thus extended this widely applied knowledge in STUMP by adding MP fate processes.
- Provide a flexible tool: the same modelling tool should be able to simulate different BMPs, facilitating the assessment of PP control strategies. The STUMP model thus extends the Universal Stormwater

Treatment Model (Wong et al., 2006) implemented in MUSIC, which is capable of simulating different treatment units.

- The quantification of result uncertainty is an essential step in order to define the range of applicability, the benefits, and the limitation of STUMP, enabling a reliable application of this model. This is also important to corroborate the main assumptions made in STUMP, which rely on general and non site-specific information (substance's inherent properties) and non PP-related measurements (flow and TSS) to represent a specific treatment unit.

6.2.2. Model description

Hydraulic submodel

STUMP is formed by several two-compartment (water and sediment) CSTR (Figure 6.1), extending the flexible approach implemented in MUSIC. Examples of this flexibility are presented in **Paper IV** and **V**, where STUMP is used to simulate systems with different hydraulic characteristics: a pond with a high length-width ratio in Lilla Essingen (**Paper IV**), a pond with a low length-width ratio, which promotes hydraulic short-circuiting, in Albertslund (**Paper V**), and a biofilter (**Paper IV**).

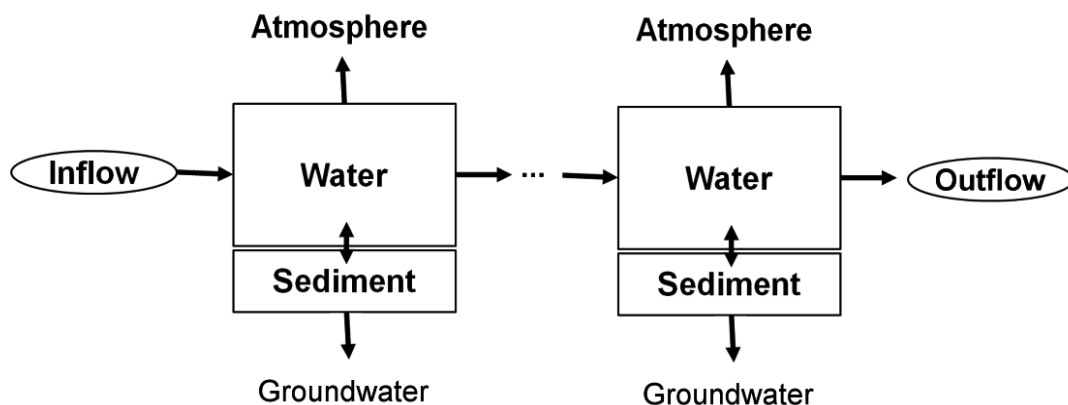


Figure 6.1. Scheme of the multi-tank structure of STUMP and connection with other environmental compartments (from **Paper IV**).

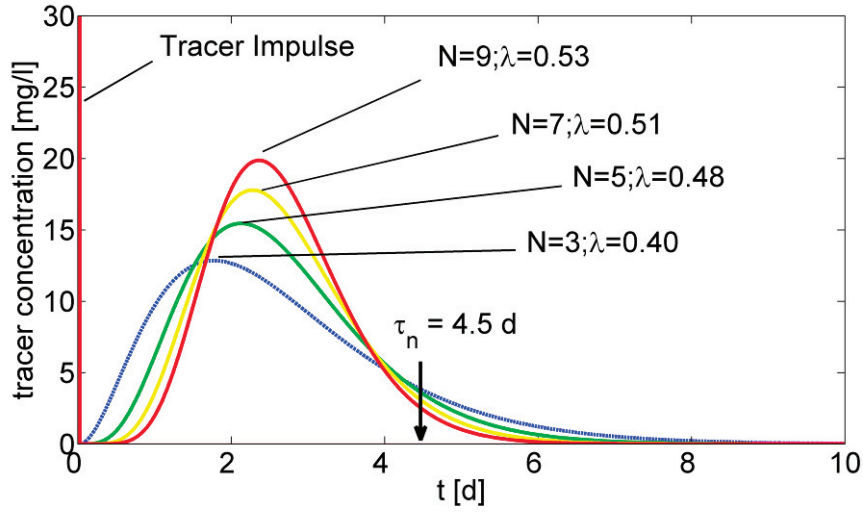


Figure 6.2. Example of outlet concentration for Basin K with different number N of serial tanks ($e_v=0.6$).

The number of tanks N can be defined without the need of flow measurements, as exemplified for the Albertslund retention pond (simulated in **Paper V**). The pond has a rectangular layout with a low length-width ratio that promotes hydraulic short-circuiting. Jansons et al. (2005), by using a CFD model, estimated a λ of 0.3 and an effective volume ratio of 0.6 for such layout, which can be reproduced by 2 serial tanks. The hydraulic efficiency for a STUMP model with 2 tanks is 0.299, which is consistent with the theoretical value.

The outlet from the tank is calculated by using the following formula:

$$\begin{aligned} Q_{out} &= K(h - h_{outlet})^\beta && \text{for } h > h_{outlet} \\ Q_{out} &= 0 && \text{for } h < h_{outlet} \end{aligned} \quad (6.2)$$

where K [$\text{m}^{3/\beta}$] and β [-] are coefficients that can be defined according to the physical structure of the simulated unit (e.g. submerged outlet, weir outlet, etc.); h [m] is the water level in the unit and h_{outlet} [m] is the threshold water level for discharge from the unit. STUMP can also simulate infiltration through the bottom of the unit by applying Darcy's law:

$$Q_{inf} = k_{bottom} \cdot \frac{A \cdot (h + h_{bottom})}{h_{bottom}} \quad (6.3)$$

where k_{bottom} [m/s] is the hydraulic conductivity of the bottom of the pond; A [m^2] is the tank surface and h_{bottom} [m] is the depth of the infiltration layer below the unit.

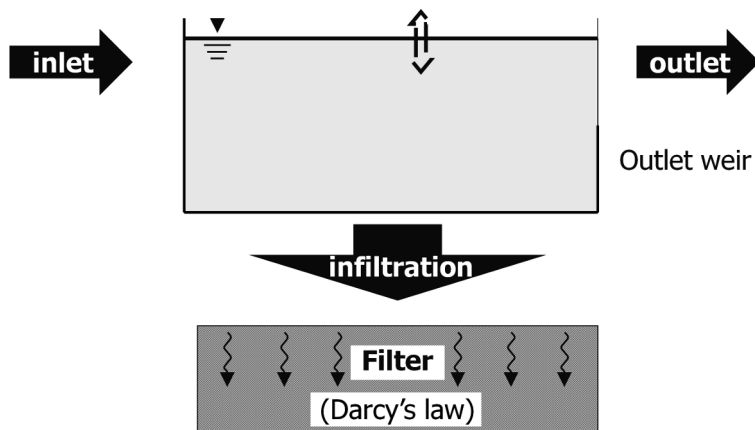


Figure 6.3. STUMP hydraulic conceptual model for a single two-compartment tank.

The hydraulic conductivity of the unit bottom can change during the simulation due to sediment accumulation and clogging of the bottom layer. This feature allows long term simulation of stormwater infiltration systems, whose performances are affected by clogging processes (e.g. Le Coustumer and Barraud, 2007).

Quality submodel

Different processes are modelled in the two compartments (Figure 6.4) that compose each serial tank (e.g. sediments are commonly assumed in anaerobic conditions, while water is considered aerobic). The fate processes included in the model are selected according to their relevance, representing a compromise between wishing to simulate all relevant processes for a very large number of stormwater pollutants while avoiding an overly complicated model. The processes included in the model are: settling and resuspension, volatilization, sorption and desorption, hydrolysis, photodegradation, and aerobic and anaerobic degradation (see Table 1 in **Paper II**).

The equations used to model these processes are selected according to the information generally available on the MPs inherent properties (Table 2 in **Paper II**). The volatilization process, for example, can be modelled by using parameters such as the substance diffusivity, the atomic diffusion volumes, the molal volume, etc.; but all these properties can be difficult to retrieve when dealing with substances that can potentially be found in stormwater. The volatilization process is thus modelled by using the relationship proposed by Trapp and Harland (1995), which is based on the substance molecular weight (easily available in existing databases).

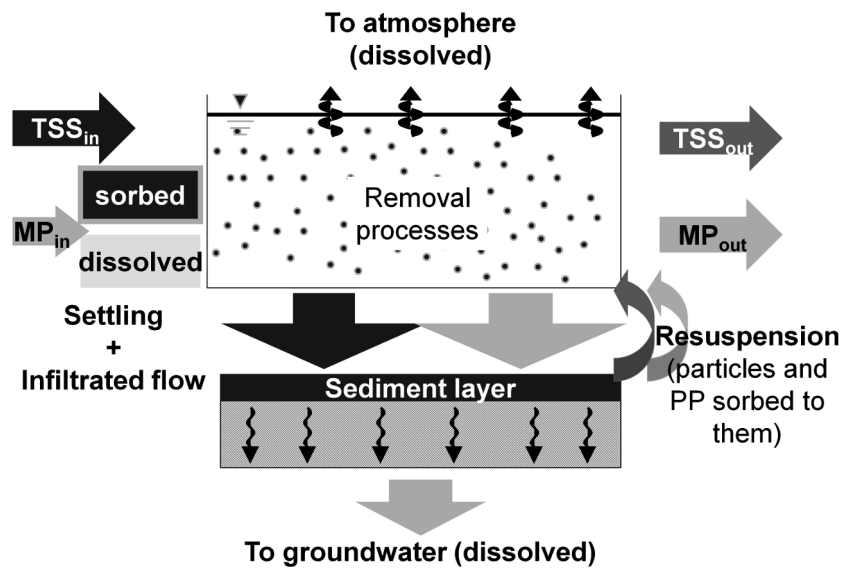


Figure 6.4. STUMP conceptual model for MP fate processes in a single two-compartment tank (from **Paper II**).

The majority of the fate processes are modelled by using pseudo-first order kinetics (as the majority of the process rates available in databases are expressed as half-lives), with the greater fraction affecting the dissolved phase (S_{MP}) and only adsorption/desorption and settling/resuspension affecting the particulate phase (X_{MP}).

The equilibrium between the two phases is strongly related to the TSS fraction (X_{TSS}) and its processes (settling/resuspension): modelling of TSS is however eased by the knowledge from existing models (with several equations and modelling approaches proposed in literature to simulate these processes) and by the relatively high amount of available measurements.

6.3. Analysis of model performance

The model performance needs to be evaluated for substances with different properties and in different typologies of stormwater treatment systems. Two different types of stormwater treatment systems are modelled in the thesis and the fate of different substances is simulated (Table 6.2), ranging from heavy metals (with only settling/resuspension and adsorption/desorption processes included in the simulations) to organic substances (with a wider range of fate processes included in the simulations). The assessment of the STUMP performance is obviously affected by the scarcity of stormwater MP measurements, i.e. the organic substances are simulated by using literature values for concentrations in stormwater runoff.

Table 6.2. Scheme of the various situations where the STUMP model performance is assessed.

Stormwater treatment unit	Stormwater Pollutant	
	Heavy metals	Organic MP
Biofilter	Paper IV	-
Retention pond	Paper IV	Paper III

6.3.1. Identification of important factors

The STUMP model is characterized by a significant number of model factors (inputs and parameters) that can affect the estimation of MP fate in the treatment unit. To enable a wide application of this model it is necessary to investigate the behaviour of the model and the influence of the various model parameters.

This information can be obtained by variance decomposition methods (see Section 3.4.1), but these approaches can be computationally demanding for STUMP, which is more complex than the runoff quality model assessed in Section 5.3. The important factors in STUMP are thus identified by using the Elementary Effects method, as the information provided by this method is regarded as sufficient to provide a good overview of the model behaviour.

To ensure that the results are not influenced by the properties of the simulated substances (e.g. substance with high tendency to sorb will stress the importance of TSS-related processes), the analysis is performed on substances with distinctly different and clearly identifiable environmental fate. The results from this analysis can thus be generalized and ensures that STUMP can confidently be used to estimate MP fate (and thus removal) of a wide range of stormwater MP in stormwater BMPs.

Table 6.3. Organic substances simulated and their expected fate in the environment based on their inherent properties.

Substance	CAS number	Expected environmental fate	Main source for stormwater
IPBC	85045-09-6	Water phase (does not undergo relevant fate processes)	Building materials (used as biocide)
Benzene	71-73-2	Atmosphere (highly volatile)	Combustion processes
Glyphosate	1071-83-6	Biodegraded	Gardening (used as biocide)
Pyrene	129-00-0	Sediments (high tendency to sorb)	Combustion processes

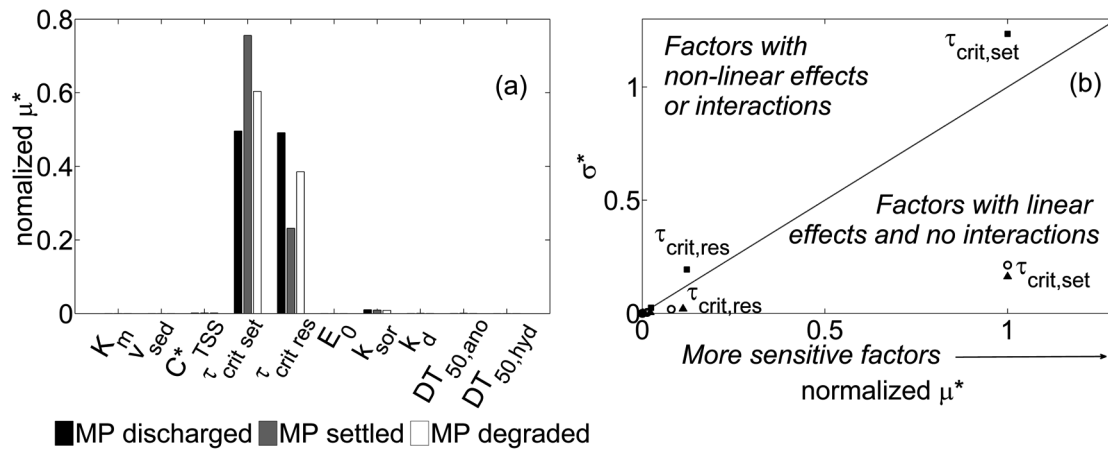


Figure 6.5. Elementary effect indices estimated for IPBC (from **Paper III**): comparison between μ^* calculated for different model outputs (a), and comparison between μ^* and σ^* (b).

The STUMP model is tested by simulating the fate of the organic substances listed in Table 6.3 (along with Cu and Zn) in a small retention pond located in Lilla Essingen, Stockholm (Sweden). An example of the results of the elementary effect analysis for IPBC is shown in Figure 6.5: the two parameters driving the settling/resuspension processes (the critical shear stresses $\tau_{crit, set}$ and $\tau_{crit, res}$) are the most sensitive (e.g. Figure 6.5a) for all the simulated substances, and they show a non-linear behaviour (e.g. Figure 6.5b).

The predominance of settling/resuspension parameters in the pond over the other parameters (driving MP fate processes) underlines the importance of TSS in the calculation of MP fate (and, consequently, in the model results uncertainty – expressed by the error bars in Figure 6.6). The estimation of MP fate in stormwater system thus requires the dynamic representation of the processes taking place in such systems.

Furthermore, the GSA suggests that results uncertainty can be reduced by using TSS measurements for calibration, which are easier to obtain and more readily available than MP data. Methods for uncertainty analysis (such as GLUE) can be used to infer TSS-related parameters and thus reduce the uncertainty in MP fate estimations, as described in **Paper III** (an example for glyphosate is shown in Figure 6.6).

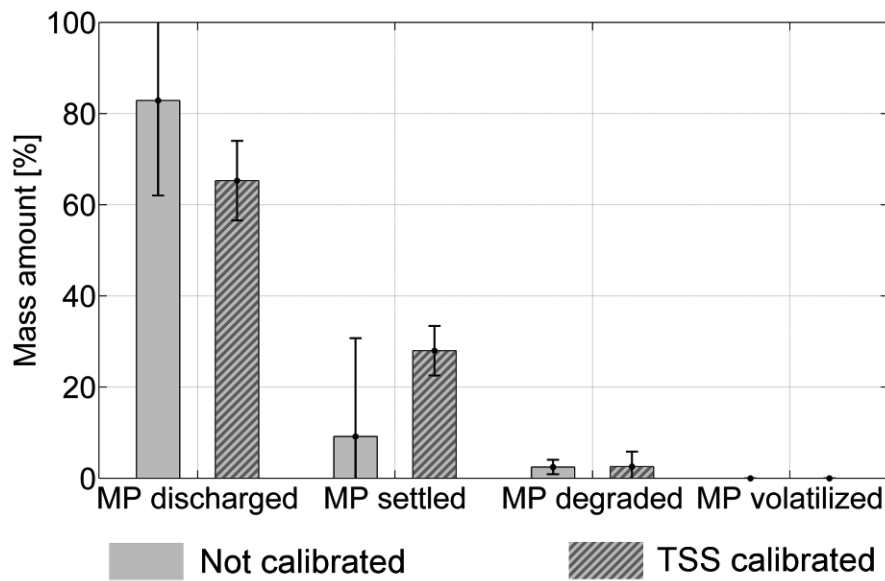


Figure 6.6. Comparison of the environmental fate for glyphosate calculated with default parameters and after the identification of parameter sets giving good TSS predictions (from **Paper III**).

The importance of non MP related processes also emerges from the GSA of the biofilter, where a significant fraction of the water volume is lost through hydrological processes (e.g. evapotranspiration, infiltration). The hydraulic parameters (h_{out} , K , k_{bottom}), which drive the outlet flow and account for hydraulic losses (using Darcy's as proxy for the other processes as evapotranspiration), thus play a relevant role for the MP fate in this unit (as shown in **Paper IV**). Result uncertainty can thus be reduced by proper simulations of the hydraulic behaviour of the unit.

The results of the GSA underline the role that a good representation of the BMP physical characteristics and of the processes that are not directly related to MP (such as TSS-related processes and hydraulic losses) plays in the estimation of MP fate. These results show how reliable estimation of MP fate can be obtained with low data requirement (e.g. literature data about substance's chemical properties), and how all the available information (e.g. TSS and flow measurements) can be exploited to reduce STUMP result uncertainty.

6.3.2. Uncertainty analysis

The quantification of STUMP result uncertainty is necessary to provide a robust basis for the application of the model. The uncertainty analysis is performed by using the available measurements or, in alternative, literature values, resembling the approach applied in chemical risk assessment. The flexibility of STUMP is tested by simulating two different stormwater treatment systems: a detention pond and a biofilter. The quality data collected in the two systems differ for their temporal resolution, with EMC values available for the retention pond and pollutographs recorded at the biofilter (see Table 3.1). This enables the assessment of the influence of input data resolution on the model results.

For both the systems the prediction bounds are estimated by using GLUE. Given the relevance of TSS processes for MP estimation identified by the GSA, a combined likelihood is used (calculated on TSS and total Cu). This ensures that behavioural parameters provide good estimation of both TSS and MP concentrations. Also, the importance of water losses in the biofilter is considered by using a combined likelihood calculated on the flow and discharged volume.

For both the simulated systems the width of uncertainty bounds for concentration predicted by STUMP (Figure 6.7 and Figure 6.8) is about the same magnitude of measurements (i.e. the ratio between the width of bounds and the measured value is around 1-1.5). The influence of the temporal resolution of input data can thus be regarded as minimal. On the other hand, input data have a relevant influence on uncertainty bounds.

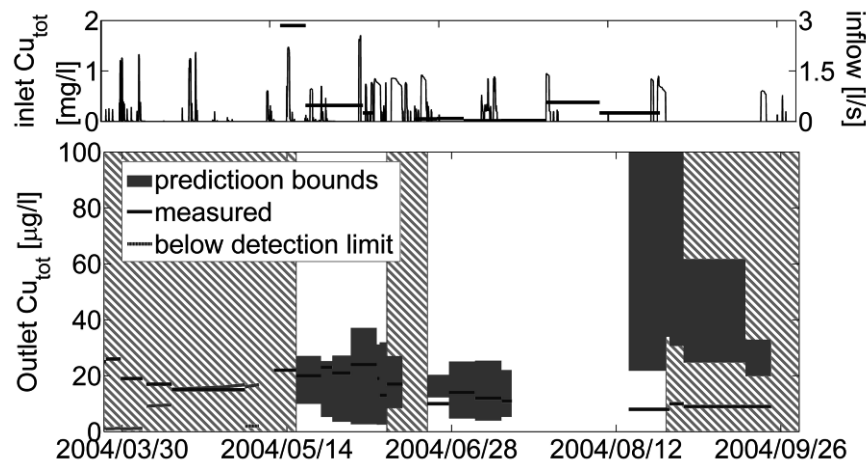


Figure 6.7. Inlet flow and measured total Cu concentrations for the retention pond (above), and measured outlet concentrations and model prediction bounds (below). Hatched areas represents periods when no inlet concentrations are available. (**Paper IV**).

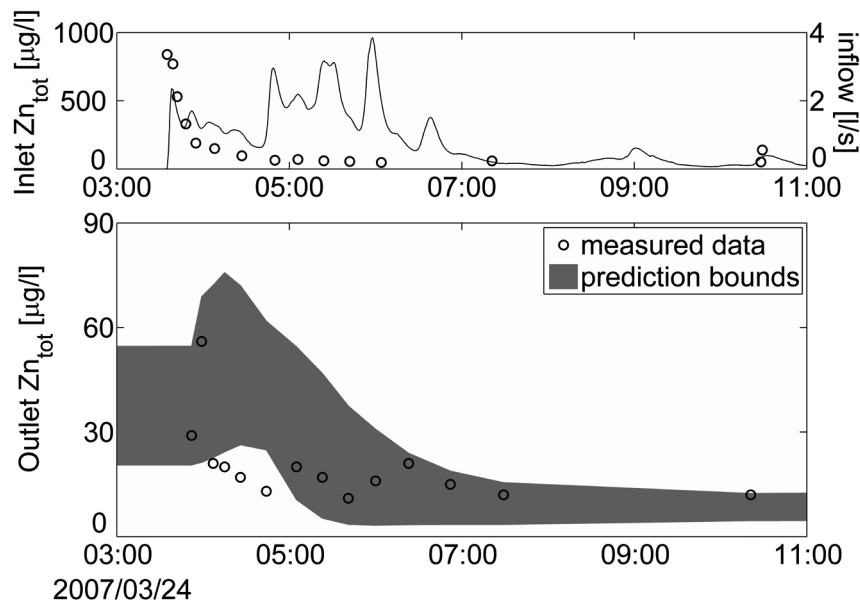


Figure 6.8. Inlet flow and measured total Zn concentrations for the biofilter (above), and measured outlet concentrations and model prediction bounds (below). (**Paper IV**).

The inlet and outlet measurements from the retention pond, for example, show temporal discrepancies, with outlet measurements taken when no inlet data were recorded, and vice versa. When no inlet concentrations are available, STUMP runs with default values (calculated from the median of observed values). These periods correspond to the intervals where STUMP uncertainty bounds are wider (e.g. Figure 6.7), with overestimation of outlet concentrations up to 420% for Zn. The width of the prediction bounds in the simulated pond is thus strongly influenced by input data.

The structural uncertainty of STUMP is highlighted by the specific characteristics of the biofilter, a system generally in dry conditions, with significant sorption processes to the biofilter medium and potential for precipitation of heavy metals.

The importance of these processes is suggested by the outlet concentrations, with a significant reduction of inlet peaks to a constant outlet concentration. STUMP underestimates sorption (as the sorption capacity of the biofilter medium is not considered) and it neglects filtration and precipitation. This structural limitation explains the pattern of the concentration prediction bounds, which fail to cover a significant number of simulations (as exemplified by the Zn simulations shown in Figure 6.8) and the underestimation of the removal efficiencies.

Table 6.4. Summary of estimated removal efficiency, expressed as mean percentage (minimum and maximum values are in brackets - from **Paper IV**).

MP	Retention pond		Biofilter	
	Measured ^a	Simulated	Measured	Simulated
Cu	80.7 (60 – 99)	39.5 (0.54 – 99.9)	48.4 ± 22.7	39.5 (0.54 – 99.9)
Zn	81.8 (57 – 99)	78.7 (0.01 – 99.9)	90.6 ± 1.89	78.7 (0.01 – 99.9)

^a expressed as monthly mean value (minimum and maximum are listed in brackets), from Stockholm Vatten (2006); ^bExpressed as value from the best behavioural parameter set and minimum and maximum values of the uncertainty bounds; ^c expressed as mean±standard deviation (Hatt et al., 2009a).

To improve the predictions of outlet concentration from the biofilter it is thus necessary to modify the STUMP conceptual model. Similarly to the findings for the runoff quality model discussed in Section 5.3.2, uncertainty decreases when looking at MP mass fluxes. The simulated removal rates for the retention pond are comparable with the values calculated from measurements (Table 6.4), while the structural limits in simulating the removal processes in the biofilter are reflected by the wide range of the simulated removal efficiencies.

The use of substance inherent properties in STUMP strengthens the application of the model also in the absence of field measurements, i.e. in a condition that is common to a great number of systems, where MP removal needs to be quantified but no measurements are available. The examples in **Paper III** (e.g. Figure 6.9) illustrate the ability of STUMP for estimating the environmental fate (and thus quantifying the potential removal) of substance with contrasting behaviour in the environment. The STUMP model provides more realistic estimations of MP removal by combining the approach commonly used in chemical risk assessment (other environmental field affected by lack of measurements) with the dynamic description of the processes taking place in stormwater treatment units. This dynamic approach can highlight and quantify potential shortcomings of treatment units (e.g. variation in the removal efficiency due to hydraulic short-circuiting, underestimation of fate processes) that could not be quantified by steady state models or by qualitative assessment.

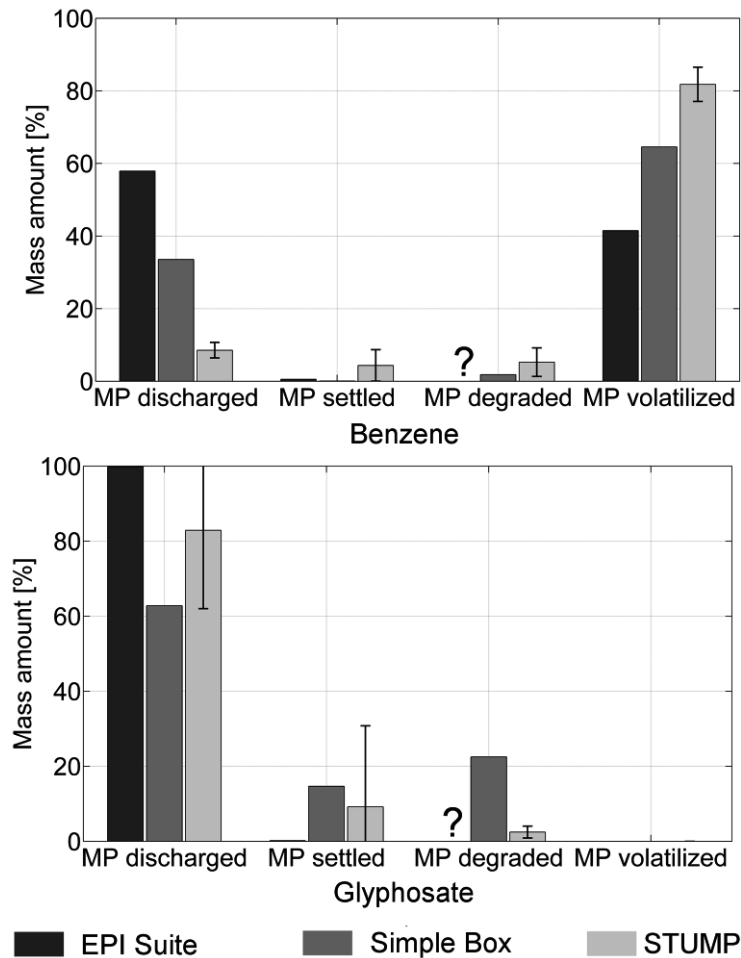


Figure 6.9. Comparison between the environmental fate estimate by STUMP and two other multimedia fate models (EPI Suite and Simple Box) for Benzene (above) and Glyphosate (below) (from **Paper III**).

The results presented in **Paper III** and **IV** show how STUMP enables the estimation of MP fate, filling a knowledge gap regarding the quantification of MP removal in stormwater treatment systems. This allows a better comparison between treatment options, allowing the identification of the most appropriate treatment for the stormwater discharged from a specific catchment. This potential application can be improved by the combination with the modelling tools described in Section 5, which can integrate missing data (reducing input data uncertainty – as in the case of the Lilla Essingen pond). Also, this integration would allow a complete assessment of different scenario for control and management of stormwater pollution caused by MP (improving e.g. the example presented in Section 5.3.3 by accounting for the BMP removal efficiency).

7. Integrated models

7.1. Theoretical background

The management of stormwater quality requires a holistic analysis and modelling of the elements of the stormwater system (as described in Sections 1.2 and 0). This requires the integration between the different models analyzed in the previous section, in order to provide a complete overview of the PP fluxes across a catchment.

Examples of integrated stormwater system models (catchment model and treatment) can be found in several studies (e.g. Freni et al., 2010) and commercial applications (see for example the review in Elliott and Trowsdale, 2007). These integrated models can provide important information that can support urban water managers, such as:

- The estimation of the PP loads discharged into the receiving waters and the identification of the major pollution sources.
- The evaluation of the pollutant loads removed by stormwater BMPs (existing or planned) and the consequent assessment of the maintenance requirements.
- The assessment of possible pollution control strategies that can be implemented to improve the ecological status downstream the modelled system.

Conversely to the increasing focus on uncertainty in integrated wastewater system models (Willems, 2008; Freni et al., 2009a; Schellart et al., 2010), the performance of integrated stormwater systems are seldom assessed. The importance that integrated models can play in the field stormwater quality management, chronically affected by lack of data, requires the consequent application of uncertainty analysis methods.

7.2. Developed approach

7.2.1. Research objectives

This section illustrated how the various approaches described in the thesis (Section 4, 5, and 6) can be merged into an integrated model. This model, combined with the statistical methods for uncertainty assessment, can be used to evaluate and compare stormwater PP control strategies.

The example presented in this section illustrates an application of the integrated model in a real context, described by data with different level of detail. This example thus represents a classical situation where some information is already available (e.g. GIS data), low-complexity measurements (e.g. flow measurements) allow an extensive description of the system, while other data (e.g. quality data) offer a limited view of the existing situation. The results of this section provide an insight on the potential and weak-points for the application of dynamic integrated models as support tools for the development and assessment of stormwater pollution control strategies.

7.2.2. Model description

The integrated model used in this example is a combination of (a) the detailed GIS catchment classification assessed in Section 4.2, (b) the stormwater quality model described in Section 5.2.2 and (c) STUMP (Section 6.2.2). The integrated model is applied in a residential-industrial catchment located in the Albertslund municipality (used also in Section 4). Stormwater is collected by a separated sewer system and discharged into a natural stream after being treated in a stormwater detention pond.

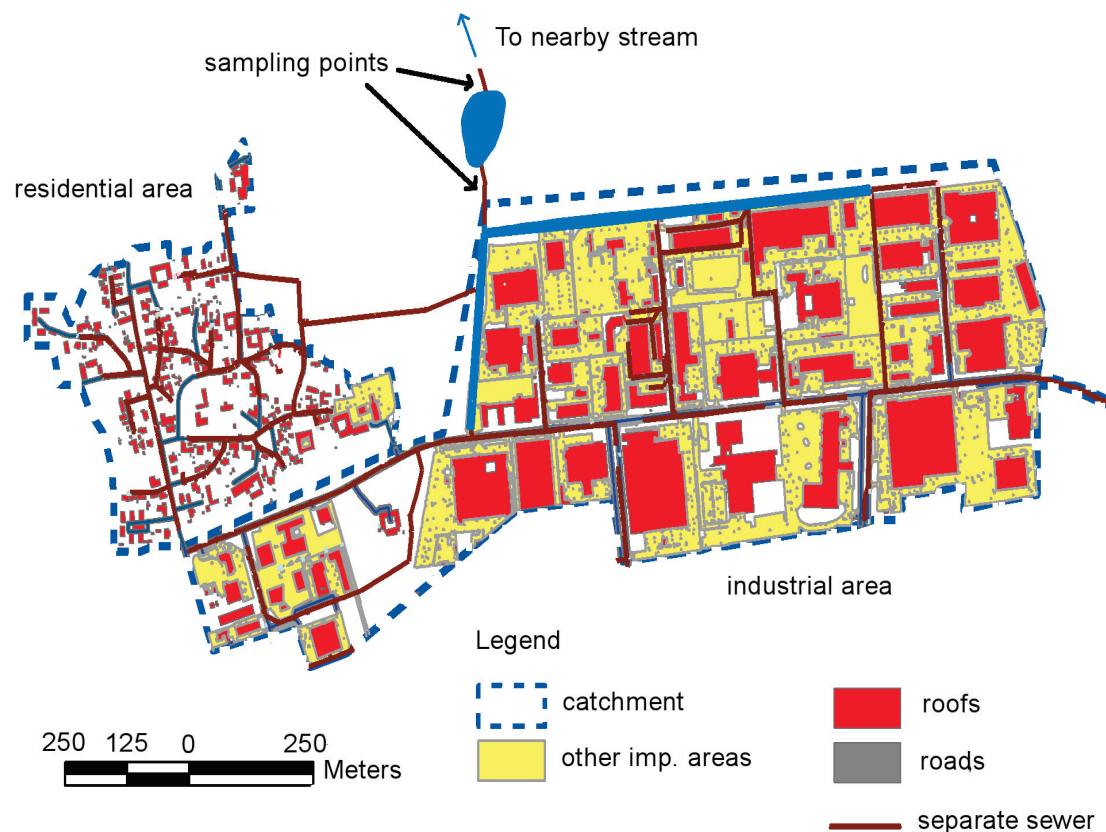


Figure 7.1. Classification of the different areas in the simulated catchment (**Paper V**).

The municipality, as part of a plan for improving the quality of the receiving water body for recreational purposes, required an assessment of stormwater PP pollution. Thus, this case represents a typical situation where the models described in the thesis can be applied as support for stormwater quality management. The catchment is subdivided into the three categories used in Section 4.2: roads, roof and other impervious areas (Figure 7.1). The classification is performed by using GIS data that are available at the municipality level, exploiting the existing information and lowering the need for the acquisition of new data.

7.3. Analysis of model performance

7.3.1. Uncertainty analysis

The behavioural parameters of the integrated model (catchment and STUMP) are identified by separately using GLUE (Section 3.4.2) for each submodel. The parameters of the hydrological submodels are identified by using flow measurements that were collected at the inlet and outlet of the pond in the period from September 2009 to October 2010 (the period from December to March is neglected as the model does not include snow melting processes). The parameters of the water quality submodels are estimated by using TSS and total Cu measurements collected at the catchment outlet for five different rain events recorded from May to October 2010.

A combined likelihood for TSS and Cu is used to evaluate the performance of each parameter set (Section 3.4.2), and the acceptance/rejection criterion is based on the fraction of observations covered by the prediction bounds (see Appendix VI for the details about the likelihood measures and acceptance thresholds).

The uncertainty of the integrated model outputs differs for the different submodels. Similarly to the results shown in Section 5.3, the catchment submodel shows significant uncertainty. The structural uncertainty of the accumulation/washoff model is emphasized by the particular characteristics of the measured data, with an intense rain event (with rainfall intensity up to about 17 $\mu\text{m/s}$ and a total precipitation of 6.4 mm) and high concentrations (up to about 1400 mg/l for TSS and 840 $\mu\text{g/l}$ for Cu_{tot}), which are likely due to resuspension of sediments in the channels upstream to the pond inlet. To better simulate this process, the exponent n (Eq. 5.1) is included in the GLUE analysis, i.e. the relationship between rainfall intensity and pollutant removal is not linear (as conversely it is assumed in Section 5.3).

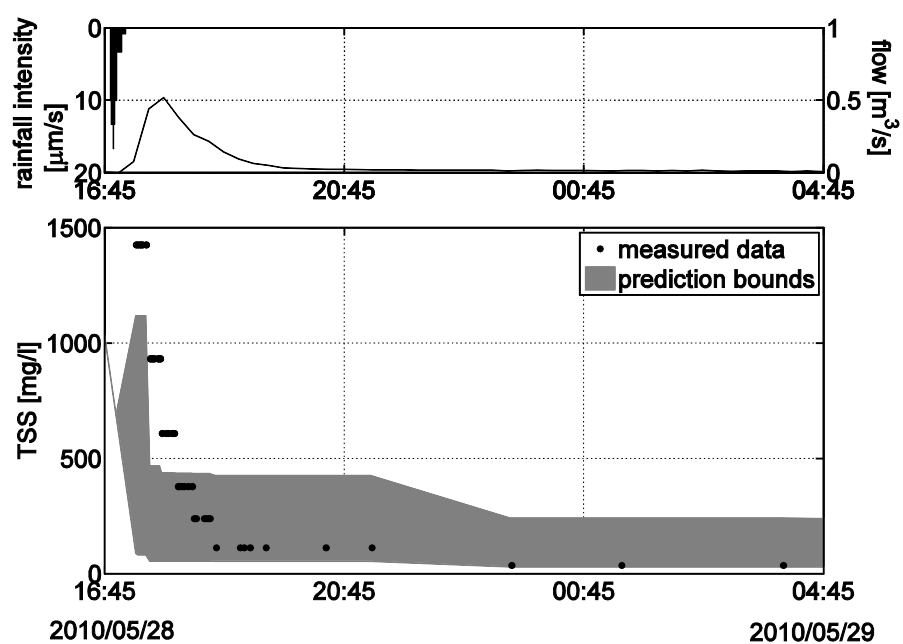


Figure 7.2. Prediction bounds for TSS concentration at the pond inlet during the event recorded on 2010/05/28.

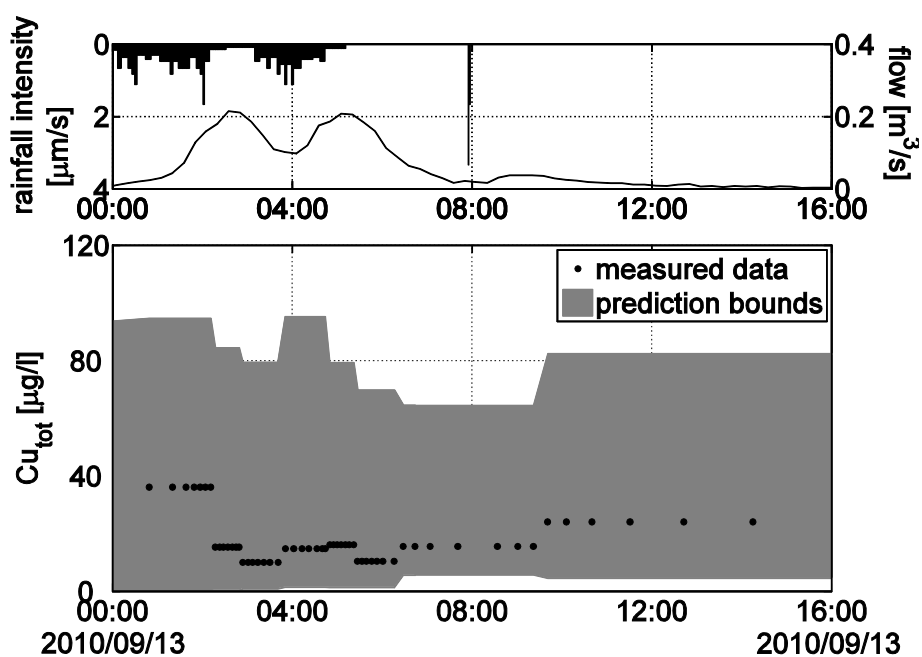


Figure 7.3. Prediction bounds for total Cu concentration at the pond inlet during the event recorded on 2010/09/13.

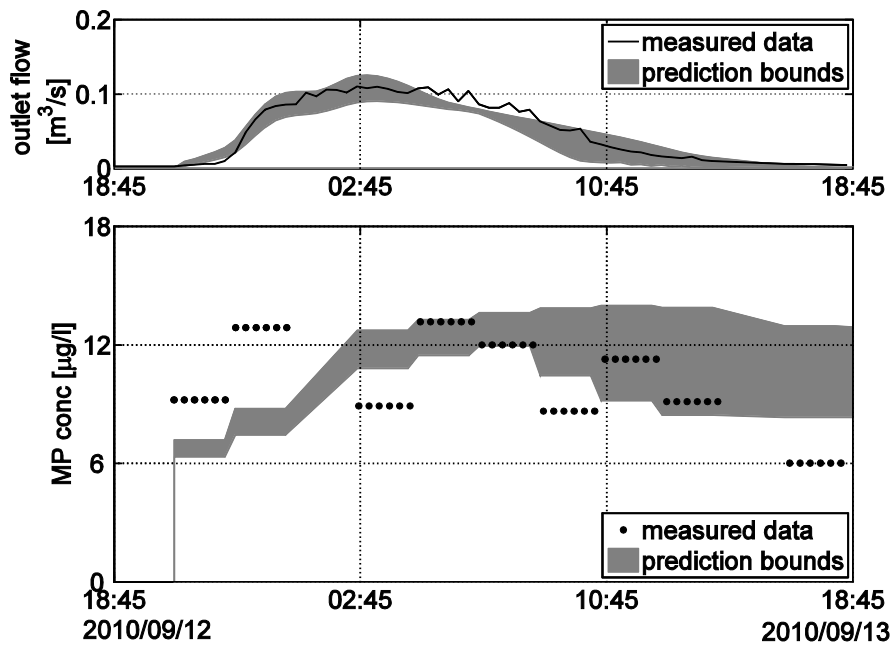


Figure 7.4. Prediction bounds for TSS concentration at the pond outlet during the event recorded on 2010/09/12.

The behavioural parameter sets are affected by this event (failing to cover all the observations - Figure 7.2) and the simulated concentrations in the runoff from the catchment are sensitive to short events with high intensity (as can be seen by the concentration bounds following the second rain event in Figure 7.3).

The estimated prediction bounds for STUMP (Figure 7.4) show a delay in the simulated peak concentration compared to measurements. This suggests that the hydraulic efficiency in the real pond is lower than simulated, with significant short-circuiting taking place during rain events. By simulating a higher hydraulic retention time τ_p than in the real system, the model is likely to overestimate the pond removal efficiency for both TSS and Cu. The efficiency of the simulated fate processes (settling and sorption), in fact, is directly proportional to τ_p , i.e. a greater fraction of untreated stormwater is discharged with shorter τ_p .

7.3.2. Uncertainty analysis in model application

Analysis of existing system

The uncertainty analysis allows the estimation of parameter sets of the integrated model that provide good estimation of the measured values. These are then used to assess the stormwater pollutant loads in the analyzed system. The annual loads (Table 7.1) are calculated by running the model using rainfall data collected in

the period 1994-2004 as input. These are characterized by significant uncertainty in the estimation of the pollutant fluxes, which is directly dependent on the high uncertainty in the calibration of the catchment runoff quality model. The uncertainty bounds of the simulated Cu loads are comparable to those estimated by using a SMC method (Figure 4.2): the simulated values include model uncertainty (which is not considered in Section 4.3), but also the information added by field measurements. GLUE, in fact, compensates the significant underestimation which is observed for the release-factor based results (Method C, as defined in Section 4.2.2) by identifying the deposition rates θ_1 (Table 5.2) that ensure better representation of the observed data.

The simulated removal efficiencies for TSS are slightly lower than those commonly reported in literature, probably due to the low hydraulic efficiency of the system. Nevertheless, the total Cu removal efficiency is within literature values (e.g. German, 2003; Bentzen, 2008; Vollertsen et al., 2009).

The simulated concentrations discharged from the pond suggest that the ELV for dissolved copper may be exceeded with high frequency. As illustrated in Figure 7.5, which shows the return period of simulated discharge event concentrations, more than 50% of the simulations exceed the ELV for dissolved Cu with a frequency higher than 10 times per year.

The existing treatment thus seems not sufficient to completely avoid short term negative effects on the ecosystem downstream the pond due to the Cu dissolved fraction. This consideration should however take into account the significant uncertainty of the catchment runoff quality submodel, which tends to overestimate Cu inlet concentration to the pond (as discussed in the previous section – see also Figure 7.3).

Table 7.1. Simulated pollutant fluxes in the catchment (minimum and maximum values are listed in brackets).

Quality parameter	Inlet to the pond	Outlet from the pond	Simulated removal efficiency [%]
TSS load [tonTSS/yr]	36.2 (7.93 – 71.9)	15.0 (3.70 – 29.5)	55.8 (40.3 – 68.7)
Cu load [kgCu/yr]	14.8 (5.36 – 37.6)	7.98 (2.21 – 23.7)	49.0 (26.5 – 59.6)
Cu _{diss} load [kgCu/yr]	-	2.53 (0.31 – 17.1)	-

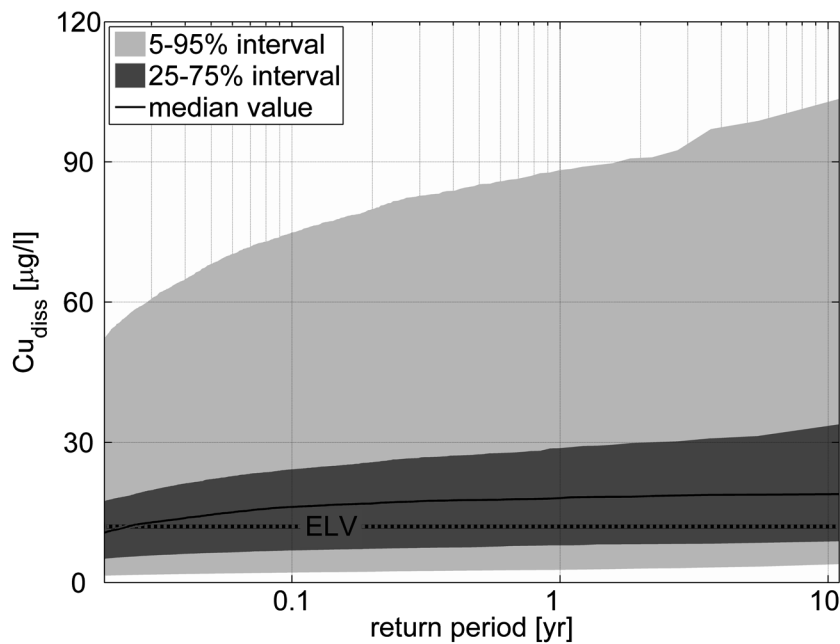


Figure 7.5. Simulated return period for dissolved Cu concentration discharged from the detention pond (discharge events are defined as coherent periods where the simulated discharge exceeds 20 l/s).

Scenario analysis

The integrated model is used to simulate two different stormwater pollution control strategies:

- *Strategy A* is based on source control and it consists of disconnection of impervious areas in the catchment (e.g. by infiltration). A disconnection of 50% of the roofs and 30% of roads and other impervious areas is assumed. This reduction corresponds to a total reduction of 40% of the catchment impervious area.
- *Strategy B* is based on improving the existing treatment by doubling the pond volume (thus doubling the hydraulic retention time) and modifying the pond layout (increasing the hydraulic efficiency λ to 0.4).

The comparison of the results for the two control strategies is presented in Table 7.2 and Figure 7.6.

The uncertainty bounds of the simulated loads (defined by the error bars in Figure 7.6) are important. Nevertheless, it is possible to analyze and compare the different scenarios. Scenario A leads to a reduction in the pollutant loads discharged to the pond.

Table 7.2. Simulated pollutant fluxes in the catchment (expressed as median - minimum and maximum values are listed in brackets).

Quality parameter	Inlet to the pond		Outlet from the pond		
	Load	Variation ^a	Load	Variation ^a	Simulated removal efficiency [%]
Scenario A					
TSS [tonTSS/yr]	29.9 (6.54 – 59.2)	-17%	9.14 (237 – 18.2)	-39%	65.70 (53.5 – 77.9)
Cu [kgCu/yr]	12.7 (4.61 – 32.3)	-14%	5.48 (1.43 – 18.6)	-31%	58.7 (32.6 – 69.4)
Cu _{diss} load [kgCu/yr]	-	-	1.96 (0.24 – 13.7)	-23%	-
Scenario B					
TSS [tonTSS/yr]	36.2 (7.93 – 71.9)	0%	10.1 (2.76 – 19.2)	-33%	68.8 (57.9 – 79.8)
Cu [kgCu/yr]	14.8 (5.36 – 37.6)	0%	6.28 (1.60 – 22.0)	-21%	59.4 (30.2 – 70.7)
Cu _{diss} load [kgCu/yr]	-	-	2.56 (0.32 – 17.0)	+1%	-

^a estimated from the median value of the baseline scenario

Also, the smaller impervious area reduces the hydraulic loads to the pond, improving the removal efficiency due higher hydraulic retention time τ_p in the pond. Scenario B leads to about 20% reduction in the discharged Cu loads, due to an increase in the retention time τ_p . Both the scenarios achieve similar reduction in TSS loads (around 30%) and higher reduction of Cu loads (both total and dissolved) is obtained for Scenario A (Figure 7.6). This reduction is mainly due to source control: in fact Scenario B, which focuses on the improvement of settling conditions in the pond, fails to reduce the Cu dissolved fraction load. The frequency of exceedance of ELV for Cu dissolved is slightly decreased in Scenario B (see Appendix VI), mainly due to the higher hydraulic efficiency λ which decreases the outlet peaks (see for example Figure 6.2). Conversely, Scenario A causes a slight increase in the frequency of ELV exceedance. The reduction in the catchment area decreases the small discharge events, but does not affect extreme events, which are also characterized by higher Cu concentrations.

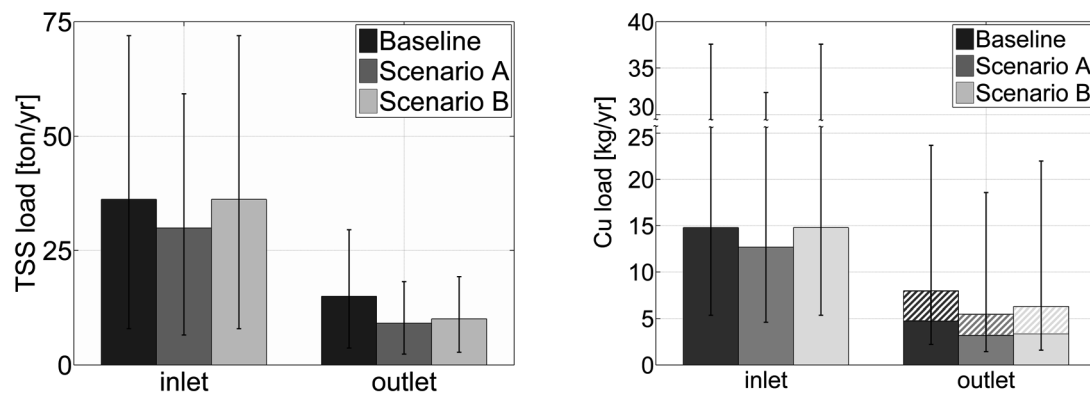


Figure 7.6. Scenario comparison for simulated pollutant loads. Hatched areas represent the dissolved fraction.

Overall, both the scenarios fail to significantly reduce the concentration peaks in the pond outlet compared to the baseline scenario. To decrease the potential risk for the aquatic environment it is thus necessary to consider additional treatments targeting the dissolved fraction (e.g. addition of flocculants or installation adsorption filters at the pond outlet).

When looking at the uncertainty bounds for the two scenarios, Scenario A shows a slight reduction in their width. This is likely to be caused by the reduction in the impervious area: the uncertainty of the catchment runoff quality submodel thus has a lower influence on the overall result uncertainty when runoff volume is reduced. Nevertheless, the significant uncertainty of the loads from the catchment prevents a clear distinction between the results of the two simulated scenarios. This stresses the need for additional measurement that would improve the identification of behavioural parameter sets while decreasing the impact of events that could be regarded as outliers. The application of integrated models for stormwater quality management thus requires an extensive description of the system, covering all the different elements of the systems (sources, drainage networks, treatment units). The limited number of quality measurements in fact strongly limits the scenario comparison. The results from Section 5.3.2 suggest that these additional runoff quality data do not necessarily require high level of detail (i.e. pollutographs), but lumped information (i.e. composite samples over long time intervals, data passive samplers) may be sufficient to reduce the uncertainty in the simulated runoff quality. These measurement techniques may also be useful to evaluate the pollution control strategies *ex-post*, i.e. to monitor the implementation and the outcomes of the chosen control strategy.

Conversely, the potential sediment resuspension processes observed in the catchment upstream the pond (Figure 7.2) may require a re-formulation of the model (e.g. by extending the use of STUMP to simulate the channel upstream the pond), with an increase in model complexity.

The results from the scenario analysis can be summarized as follows:

- Strategy A reduces the release of pollutants from the catchment and improves the removal efficiency of the pond. Both particulate and dissolved copper loads are reduced, but extreme concentration peaks are not affected.
- Strategy B improves the settling conditions in the pond, but this affects only the particulate fraction. The load of dissolved Cu is in fact unaffected compared to the baseline scenario. Extreme concentration peaks are slightly reduced due to higher dilution in the pond.
- Both the scenarios fail to satisfactorily reduce the potential risk for the aquatic environment linked to the pollutant dissolved phases. This should thus be addressed by additional solutions.
- Possible actions aiming to improve the removal in the pond should focus on sensibly improving the hydraulic efficiency λ (i.e. reducing the hydraulic short-circuiting) rather than increasing the volume of the treatment unit.
- The simulated pond removal efficiency is similar for both the analyzed scenarios, but the source reduction applied in Scenario A implies lower sediment loads accumulated in the pond (with consequent lower pond maintenance costs).
- Overall, the source control strategy (Scenario A) seems to obtain greater improvements in terms of Cu loads discharged from the Albertslund catchment with lower uncertainty.

The example presented in this Section illustrates how the integrated model can be used for comparing different scenario in stormwater quality management.

The combination with uncertainty analysis methods highlights the major sources of uncertainty and recognizes the areas which require additional data. This demonstrates how the various modelling approaches presented in the thesis and integrated in this section can support urban water managers.

8. Discussion

This thesis presents a great number of results covering different elements of the stormwater system, and techniques and methodologies used to model stormwater micropollutants. These results are below synthesized and discussed in respect of the basic research questions that are listed in Section 2.

How can pollutant sources be characterized? How can the distribution of micropollutant sources across the catchment be represented?

Stormwater PP sources are characterized by a significant spatial variability, which can only be represented by using a detailed representation of the study area. The detail of source characterization is clearly conditional on data availability, and a more detailed representation of the land usage ensures a better representation of PP sources. Although the major source of uncertainty in the calculation of loads is on the representativeness of the used dataset with respect to the study area and sampling period (i.e. the ability to represent the pollutant sources in the catchment), rather than the level of detail of catchment characterization, a higher detail allows the identification of the major PP sources. However, the presence of non-identified PP sources in the catchment can represent a significant source of uncertainty. In the study area shown in Section 4, for example, a clear underestimation of copper loads released from roofs is suggested by comparing measurements with calculated loads. These results highlight the need for a better classification of pollutant sources or a better quantification of release factors from these sources.

Is it possible to simulate the complex dynamic processes that drive the release of micropollutants into stormwater and their transport across the stormwater system?

The complexity of the processes driving PP release and transport in stormwater systems is such that all the available models encounter difficulties in providing robust and reliable estimation of PP loads and concentrations. However, the results of this project show that the combination of statistical methods for uncertainty analysis with a simple conceptual dynamic model can provide results that can be used as support for the elaboration of stormwater pollution control strategies (e.g. Section 5.3.3 and 7.3.2). These statistical methods are necessary to gain a complete knowledge about the behaviour of the model and its parameters. This information is subsequently used to estimate the model result uncertainty by using a limited number of prior assumptions. This is relevant in the stormwater quality field, which is characterized by a significant uncertainty

level (which according to the terminology introduced by Walker et al. (2003), sometimes resembles ignorance). However, the application of these uncertainty estimation techniques may require important computational resources and good modelling and mathematical skills. The techniques applied in the project aimed to reduce the computational resources (e.g. the SCEM-UA algorithm) and to reduce the need for complex mathematical formulations (e.g. the use of informal likelihood measures). The uncertainty of pollution loads estimated in the examples is in the range of 50-60%. This uncertainty is comparable with the magnitude of measurement errors (e.g. stormwater sampling error) and it does not seem to depend on the time resolution of the measured data. Thus, the combination of the analyzed models with uncertainty estimation methods allows their use for estimating PP fluxes.

What are the fate processes that should be considered to quantify the PP removal in stormwater treatment systems? How can these processes be modelled in different stormwater treatment systems?

The fate (and the removal) of micropollutants in stormwater treatment systems can be represented by modelling the processes that are commonly included in chemical fate models (e.g. volatilization, biodegradation, hydrolysis, sorption, photodegradation) and affect the particulate and dissolved phase of the pollutant. This approach is based on the chemical properties of the modelled substance and it thus exploits information that is commonly accessible (and that sometimes represent the only available information). The peculiar characteristics of stormwater treatment systems, with highly dynamic processes depending on the rainfall pattern, require the application of dynamic models that are capable of representing the specific behaviour of the modelled system (e.g. the hydrodynamic of the system and its influence on TSS). The STUMP model includes these issues by coupling chemical fate models with widely applied stormwater treatment models that are capable of simulating macropollutants. This developed approach benefits of all the available information (chemical properties, flow and macropollutant measurements) and reduces the need for extensive monitoring campaigns by decreasing the dependence on PP field measurements. This feature, combined with the ability of representing different typologies of stormwater treatment facilities, enables a wide application of models as tools to assess the performance of various BMP.

How can PP fluxes across stormwater systems be modelled?

The combination of the modelling approaches investigated and developed in the thesis allows the estimation of PP fluxes across the entire stormwater system. The integration of these models is conditional on the assessment of model result uncertainty. Uncertainty analysis can highlight the issues that need to be addressed to improve the reliability of the results (e.g. measurement of additional environmental parameters). The analysis of the simulated PP fluxes can support the elaboration of pollution control strategies by underlining the areas for potential improvements (e.g. source control, improvement of existing treatment facilities, additional removal processes that need to be included in the system). The flexibility of the model allows the identification of these strategies according to the different characteristics of each modelled substance (sources, environmental behaviour, etc.).

Is it possible to simulate the effects of potential pollution control strategies on the existing situation?

The integrated stormwater quality model illustrated in Section 7 can simulate the PP fluxes in the actual system and can also be used to simulate the modifications entailed in possible pollution control strategies. The parameters and the inputs used in the various submodels (e.g. rainfall intensity, chemical properties, release factors, etc.) allow the simulation of different scenarios. The inclusion of uncertainty in the scenario comparison allows a more reliable comparison of the different options.

The results from the integrated model can also be used to plan monitoring campaigns and to define the optimal sampling design (location, sampling methodology, etc.). The example presented in Section 7.3.2 shows how the integrated dynamic models developed during the project can represent an important tool in stormwater quality management aiming to control stormwater micropollutants.

9. Conclusions

The work presented in this thesis is the first example of development and application of integrated dynamic models (simulating sources, transport and treatment) for management of stormwater Priority Pollutants which address the high spatial variability of pollutant sources, the different behaviour of stormwater PP in the environment, the wide range of choices for stormwater treatment, and the inherent uncertainty affecting model results. The thesis fills a knowledge gap due to the previous absence of modelling tools targeting these substances. The results of this thesis provide a framework for a trustworthy estimation of Priority Pollutants fluxes from the sources to the sink and it will potentially support urban water managers in their decision making processes. The main conclusions of the thesis are:

- Uncertainty analysis improves the confidence in any modelling tools, including those developed in this thesis for stormwater quality management. The identification of uncertainty source (by using GSA) and the quantification of result uncertainty (by using methods which requires a limited number of assumptions, such as GLUE) is an essential procedure to rationalize the modeller's resources and to provide trustworthy results when dealing with stormwater PP. The final users (urban water managers) are able to interpret the model results based on the estimated level of uncertainty. Thus, modelling of stormwater PP cannot be detached from uncertainty analysis.
- Among the possible approaches, a detailed level of catchment characterization, which can employ information stored in Geographical Information Systems, is more suitable to deal with the high spatial variability of PP sources. This characterization enables the detection of significant sources of PP and highlight potential investigations that could reduce results uncertainty (additional estimation of release factors, improved characterization of the catchment) but it does not reduce the uncertainty linked to non-identified sources.
- Dynamic continuous models can be used to estimate PP loads. The combination with uncertainty analysis techniques, which identify the major sources of uncertainty and quantify model prediction bounds, allows the use of these models for scenario analysis in practice despite their significant level of uncertainty (around 60% of the measured

values). It is thus possible to employ these tools to simulate the dynamic processes behind stormwater pollution over long time periods, while at the same time being aware of the involved uncertainty.

- The fate of stormwater PP in stormwater treatment systems can be modelled by considering the inherent properties of the modelled substances. The developed model (STUMP), based on the combination of existing dynamic conceptual models for stormwater treatment with the mathematical formulations commonly applied in chemical risk assessment, provides reliable estimation of PP removal. This is confirmed by the simulated width of prediction bounds in the outlet concentrations, which are of similar magnitude of observed values. Also, the use of substance's inherent properties reduces the need for PP measurements, as the major sources of uncertainty are related to a correct simulation of the physical characteristic of the treatment unit. Thus, results uncertainty can be reduced by using easily obtainable measurements.
- Integrated conceptual dynamic models allow the quantification of PP fluxes across stormwater systems. The proposed approach (detailed catchment characterization based on GIS data, dynamic conceptual models, and use of substance's inherent properties to estimate the fate of micropollutants) represents a compromise between model complexity, available information, level of uncertainty and purpose of the model. Also, the integration of submodels allows the evaluation of the potential impact of stormwater discharge on the aquatic environment, and the evaluation of different scenarios for reduction of PP discharges. The integrated model is thus a useful tool for the subjects (urban water managers) involved in stormwater quality management.

10. Suggestions for future work

Researchers try to find answers and solutions to scientific problems, but they often raise more questions and highlight new areas that need to be investigated. This thesis does not represent an exception, as the presented results cover only a limited area of the wide and complex field of stormwater quality modelling.

The investigation of the study areas during the project leaves several open questions:

- *What information is necessary to reproduce the spatial variability of PP sources and reduce the uncertainty in the pollutant loads estimation?* This is mostly relevant for organic substances (as the thesis mainly addresses pollutants in the particulate form) released from point sources and spread across the catchment (e.g. from industrial activities, etc.). Ideally, a detailed field investigation (e.g. on-site inspection) should be able to map and catalogue all the PP sources in the study area, but this operation is very time consuming. The results from this thesis highlight how a detailed characterization provides better results for diffuse sources, such as traffic and building materials. Future research should investigate if a similar approach can be extended to other sources (point and diffuse) and which information (maps, list of activities, etc.) is necessary to obtain a reliable estimation of PP release in the catchment.
- *What is the optimal level of complexity necessary to simulate PP release and transport?* The project investigated the ability of dynamic conceptual models to simulate stormwater quality. Future research should compare these results (including their uncertainty) with those generated by model with different level of complexity identified in Section 5.1 (e.g. stochastic models, regression models, etc.).
- *Are the current models capable of representing the release and transport of dissolved pollutants?* The current accumulation/washoff formulation applied in a great number of stormwater quality models (including those investigated in this study) represents pollutants as particles. Future research should identify the mathematical formulation that ensures a better representation of the release of dissolved substances (e.g. release of metals from corrosion of metal roofs, leaching of organic biocides from building material, etc.) and of their transport (considering e.g.

speciation into particulate and dissolved phase in the drainage network), similarly to the approach applied in STUMP.

- *What level of detail in measurements is necessary to optimize model performance?* The performance of the various water quality models developed during the project were usually compared against flow- or time-proportional composite samples. The collection of these samples commonly encounters several difficulties (technical, financial, etc.) and results from this thesis suggest that the time resolution of the measurements does not significantly affect the uncertainty bounds. Future research should address the use of information with a lower level of detail (e.g. EMC, observation from passive samplers covering several events, etc.) for the identification of model parameters and their effect on model prediction bounds.
- *What is the uncertainty in the prediction of loads and removal of organic micropollutants in stormwater BMPs?* The quantification of the uncertainty in prediction of organic MP in stormwater treatment systems was limited by the number of available measurements. Future research, based on additional field measurements, should complete the work presented in this study by quantifying STUMP results uncertainty for these substances.
- *What is the uncertainty of STUMP when applied in different BMPs?* The lack of data did not only impede the assessment of STUMP performance for organic substance, but also limited the evaluation of STUMP performance in different treatment units to a couple of BMP (retention ponds and biofilter). Future research should expand the results obtained during the project by simulating a wider range of stormwater treatment typologies (e.g. settling tanks, infiltration basins, filtration systems, etc.).
- *Is it possible to validate the calculated prediction bounds?* The prediction bounds that are estimated throughout the thesis are based on the ability of covering the available observations. Additional independent data (i.e. not used in the uncertainty analysis) should be used to “validate” the prediction bounds, i.e. the ability of prediction bounds to cover independent observations should be assessed. Also, the definition of the acceptability threshold (i.e. how many observations a “good” model needs to cover?) requires a robust framework which, acknowledging the impossibility of stormwater quality models to cover

all the observed data, aims to reduce the subjectivity in this step of GLUE. This research can be extended to other fields of environmental modelling.

- *What are all the sources of uncertainty affecting the application of models for stormwater quality management?* The uncertainty investigated in this thesis include only a part of the locations, levels and natures (according to the classification introduced by Walker et al., 2003; and further extended by Warmink et al., 2010) potentially involved in model-based stormwater quality management. Future research should integrate the results of this thesis by finalizing the identification and classification of the various sources of uncertainty neglected in this study.
- *How can the models developed in the thesis be integrated in a user-friendly interface?* The models developed in the thesis are developed by using licensed software (MATLAB[®] and WEST[®]): this strongly limits their application to the academic world, given the limited diffusion of this licensed software among practitioners. To allow a wider application of the developed models, these should be coded in other simulation platforms (e.g. existing software for stormwater modelling, or in an open source language). This is a key point to allow the subjects involved in stormwater management (practitioners, urban water managers) to fully benefit from the outcomes of this thesis.

11. References

- Ackerman, D., Stein, E. D. (2008). Evaluating the effectiveness of best management practices using dynamic modeling. *Journal of Environmental Engineering*, **134**(8), 628-639.
- Ahlman, S. (2006). *Modelling of substance flows in urban drainage systems*. PhD Thesis, Chalmers University of Technology, Göteborg, Sweden.
- Alley, W.M. (1981). Estimation of impervious-area washoff parameters. *Water Resources Research*, **17**(4), 1161-1166.
- Alley, W.M., Smith, P. E. (1981). Estimation of accumulation parameters for urban runoff quality modelling. *Water Resources Research*, **17**(6), 1657-1664.
- Avellaneda, P., Roseen, R. M., Ballester, T. P., Houle, J. J. (2009). On parameter estimation of urban storm-water runoff model. *Journal of Environmental Engineering*, **135**(8), 595-608.
- Bach, M., Letzel, M., Kaul, U., Forstner, S., Metzner, G., Klasmeier, J., Reichnberger, S., Frede, H. G. (2010). Measurement and modeling of bentazone in the river Main (Germany) originating from point and non-point sources. *Water Research*, **44**(12), 3725-3733.
- Ball, J.E., Jenks, R., Aubourg, D. (1998). An assessment of the availability of pollutant constituents on road surfaces. *Science of the Total Environment*, **209**(2-3), 243-254.
- Barbé, D.E., Cruise, J. F., Mo, X. (1996). Modeling the build-up and washoff of pollutants on urban watersheds. *Water Resources Research*, **32**(3), 511-519.
- Baun, A., Eriksson, E., Ledin, A., Mikkelsen, P. S. (2006). A methodology for ranking and hazard identification of xenobiotic organic compounds in urban stormwater. *Science of the Total Environment*, **370**(1), 29-38.
- Behera, P.K., Adams, B. J., Li, J. Y. (2006). Runoff quality analysis of urban catchments with analytical probabilistic models. *Journal of Water Resources Planning and Management*, **132**(1), 4-14.
- Benedetti, L., Vezzaro, L., Gevaert, V., De Keyser, W., Verdonck, F., De Baets, F., Nopens, I., Vanrolleghem, P.A., Mikkelsen, P.S. (2009). Dynamic Transport and Fate Models for Micro-Pollutants in Integrated Urban Wastewater Systems. In: *Proc. WEFTEC 09, 82nd Annual Water Environment Federation Technical Exhibition and Conference*, Orlando, Florida, USA, October 10-14, 2009.
- Bentzen, T. R. (2008). *Accumulation of pollutants in highway detention ponds*. PhD Thesis, Aalborg University, Aalborg, Denmark.
- Bertrand-Krajewski, J.L. (2007). Stormwater pollutant loads modelling: Epistemological aspects and case studies on the influence of field data sets on calibration and verification. *Water Science and Technology*, **55**(4), 1-17.

- Bertrand-Krawjewski, J.L., Briat, P., Scrivener, O. (1993). Sewer sediment production and transport modelling: a literature review. *Journal of Hydraulic Research*, **32**(4), 435-460.
- Bertrand-Krawjewski, J.L., Bardin, J.-P. (2002). Evaluation of uncertainties in urban hydrology: Application to volumes and pollutant loads in a storage and settling tank. *Water Science and Technology*, **45**(4-5), 437-444.
- Beven, K.J. (2006). A manifesto for the equifinality thesis. *Journal of Hydrology*, **320**(1-2), 18-36.
- Beven, K. J. (2009). *Environmental Modelling: An Uncertain Future?* Routledge, London, UK.
- Beven, K., Binley, A. (1992). Future of distributed models: Model calibration and uncertainty prediction. *Hydrological Processes*, **6**(3), 279-298.
- Beven, K.J., Freer, J. E. (2001). Equifinality, data assimilation, and uncertainty estimation in mechanistic modelling of complex environmental systems using the GLUE methodology. *Journal of Hydrology*, **249**(1-4), 11-29.
- Beven, K.J., Smith, P., Freer, J. E. (2008). So just why should a modeller choose to be incoherent? *Journal of Hydrology*, **354**(1-4), 15-32.
- Blasone, R.S., Madsen, H., Rosbjerg, D. (2008a). Uncertainty assessment of integrated distributed hydrological models using GLUE with Markov chain Monte Carlo sampling. *Journal of Hydrology*, **353**(1-2), 18-32.
- Blasone, R.S., Vrugt, J. A., Madsen, H., Rosbjerg, D., Robinson, B. A., Zyvoloski, G. A. (2008b). Generalized Likelihood Uncertainty Estimation (GLUE) Using Adaptive Markov Chain Monte Carlo Sampling. *Advances in Water Resources*, **31**(4), 630-648.
- Bujon, G., Herremans, L., Phan, L. (1992). Flupol: A forecasting model for flow and pollutant discharge from sewerage systems during rainfall events. *Water Science and Technology*, **25**(8), 207-215.
- Burkhardt, M., Junghans, M., Zuleeg, S., Boller, M., Scoknecht, U., Lamani, X., Bester, K., Vonbank, R., Simmler, H. (2009). Biozide in Gebäudefassaden - ökotoxikologische Effekte, Auswaschung und Belastungsabschätzung für Gewässer; Biocides in building facades - ecotoxicological effects, leaching and environmental risk assessment for surface waters (in German). *Umweltwissenschaften und Schadstoff-Forschung*, **21**(1), 39-47.
- Campolongo, F., Cariboni, J., Saltelli, A. (2007). An effective screening design for sensitivity analysis of large models. *Environmental Modelling and Software*, **22**(10), 1509-1518.
- Carstensen, J., Vanrolleghem, P. A., Rauch, W., Reichert, P. (1997). Terminology and methodology in modelling for water quality management - a discussion starter. *Water Science and Technology*, **36**(5), 157-168.

- Chan, K., Tarantola, S., Saltelli, A., and Sobol', I. M. (2004). Variance-Based Methods. In: *Sensitivity Analysis*, Saltelli, A., Chan, K., and Scott, E. M. (eds.), John Wiley & Sons, Chichester, UK.
- Charbeneau, R.J., Barret, M. E. (1998). Evaluation of methods for estimating stormwater pollutant loads. *Water Environment Research*, **70**(7), 1295-1302.
- Chen, J., Adams, B. J. (2006). Analytical urban Storm Water quality models based on Pollutant and washoff processes. *Journal of Environmental Engineering*, **132**(10), 1314-1330.
- Chen, J., Adams, B. J. (2007). A derived probability distribution approach to stormwater quality modelling. *Advances in Water Resources*, **30**(1), 80-100.
- Clark, S.E., Steele, K. A., Spicher, J., Siu, C. S., Lalor, M. M., Pitt, R., Kirby, J. T. (2008). Roofing materials' contributions to storm-water runoff pollution. *Journal of Irrigation and Drainage Engineering*, **134**(5), 638-645.
- Corominas, L., Rieger, L., Hauduc, H., Vanrolleghem, P. A., Takacs, I., Ekama, G., Oehmen, A., Gernaey, K. V., van Loosdrecht, M. C. M., Comeau, Y. (2010). New framework for standardized notation in wastewater treatment modelling. *Water Science and Technology*, **61**(4), 841-857.
- Danish Ministry of Environment (2006). Bekendtgørelse om miljøkvalitetskrav for vandområder og krav til udledning af forurenende stoffer til vandløb, søer eller havet (Announcement on environmental quality requirements for water areas and criteria for discharge of pollutants in rivers, lakes and sea). BEK nr 1669 af 10/12/2006.
- De Keyser, W., Gevaert, V., Verdonck, F., Nopens, I., De Baets, B., Vanrolleghem, P. A., Mikkelsen, P. S., Benedetti, L. (2010). Combining multimedia models with integrated urban water system models for micropollutants. *Water Science and Technology*, **62**(7), 1614-1622.
- Deletic, A., Maksimovic, C., Ivetic, M. (1997). Modelling of storm wash-off of suspended solids from impervious surfaces. *Journal of Hydraulic Research*, **35**(1), 99-118.
- DiBlasi, C.J., Houn, L., Davis, A. P., Ghosh, U. (2009). Removal and Fate of Polycyclic Aromatic Hydrocarbon Pollutants in an Urban Stormwater Bioretention Facility. *Environmental Science and Technology*, **43**(2), 494-502.
- Dochain, D., Vanrolleghem, P. A. (2001). *Dynamical modelling and estimation in wastewater treatment processes*. IWA Publishing, London, UK.
- Dortch, M. S., Gerald, J. A. (1995). *Screening-Level Model for Estimating Pollutant Removal by Wetlands*. Report Wetlands Research Program, Technical Report WRP-CP-9, U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg, Mississippi, USA.
- Dotto, C.B.S., Deletic, A., Fletcher, T. D. (2009). Analysis of parameter uncertainty of a flow and quality stormwater model. *Water Science and Technology*, **60**(3), 717-725.

- Dotto, C.B.S., Kleidorfer, M., Deletic, A., Fletcher, T. D., McCarthy, D. T., Rauch, W. (2010). Stormwater quality models: performance and sensitivity analysis. *Water Science and Technology*, **62**(4), 837-843.
- Dotto, C.B.S., Mannina, Kleidorfer, M., **Vezzaro, L.**, Henrichs, M., McCarthy, D. T., Freni, G., Rauch, W., Deletic, A.; Comparison of different uncertainty techniques in urban stormwater quantity and quality modelling. Manuscript in preparation.
- EEA - European Environmental Agency (1999). *Environmental indicators: Typology and overview*. Report Technical report No 25, European Environment Agency, Copenhagen, Denmark.
- Egodawatta, P., Thomas, E., Goonetilleke, A. (2007). Mathematical interpretation of pollutant wash-off from urban road surfaces using simulated rainfall. *Water Research*, **41**(13), 3025-3031.
- Ekstrand, S., Östlund, P., Hansen, C. (2001). Digital Air Photo Processing for Mapping of Copper Roof Distribution and Estimation of Related Copper Pollution. *Water, Air and Soil Pollution: Focus*, **1**(3-4), 267-278.
- Elliot, A.H., Trowsdale, S. A. (2007). A review of models for low impact urban stormwater drainage. *Environmental Modelling and Software*, **16**(3), 195-231.
- Eriksson, E., Baun, A., Mikkelsen, P. S., Ledin, A. (2005). Chemical hazard identification and assessment tool for evaluation of stormwater priority pollutants. *Water Science and Technology*, **51**(2), 47-55.
- Eriksson, E., Baun, A., Mikkelsen, P. S., Ledin, A. (2007). Risk assessment of xenobiotics in stormwater discharged to Harrestrup Å, Denmark. *Desalination*, **215**(1-3), 187-197.
- European Commission (2000). Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.
- European Commission (2008). Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council.
- European Communities (2003). *Technical Guidance Document on Risk Assessment. Part II*. Report EC - Joint Research Centre, Institute for Health and Consumer Protection, European Chemicals Bureau (ECB), Ispra, Italy.
- Freni, G., Mannina, G., Viviani, G. (2009a). Uncertainty assessment of an integrated urban drainage model. *Journal of Hydrology*, **373**(3-4), 392-404.

Freni, G., Mannina, G., Viviani, G. (2009b). Urban runoff modelling uncertainty: Comparison among Bayesian and pseudo-Bayesian methods. *Environmental Modelling and Software*, **24**(9), 1100-1111.

Freni, G., Mannina, G., Viviani, G. (2010). Urban Storm-Water Quality Management: Centralized versus Source Control. *Journal of Water Resources Planning and Management - ASCE*, **136**(2), 268-278.

Gatelli, D., Kucherenko, S., Ratto, M., Tarantola, S. (2009). Calculating first-order sensitivity measures: A benchmark of some recent methodologies. *Reliability Engineering and System Safety*, **94**(4), 1212-1219.

Gaume, E., Villeneuve, J.-P., Desbordes, M. (1998). Uncertainty assessment and analysis of the calibrated parameter values of an urban storm water quality model. *Journal of Hydrology*, **210**(1-4), 38-50.

German, J. (2003). *Reducing stormwater pollution - Performance of retention ponds and street sweeping*. PhD Thesis, Chalmers University of Technology, Göteborg, Sweden.

Gevaert, V., Verdonck, F., Benedetti, L., De Keyser, W., De Baets, B. (2009). Evaluating the usefulness of dynamic pollutant fate models for implementing the EU Water Framework Directive. *Chemosphere*, **76**(1), 27-35.

Göbel, P., Dierkes, C., Coldewey, W. G. (2007). Storm water runoff concentration matrix for urban areas. *Journal of Contaminant Hydrology*, **91**(1-2), 26-42.

Grayson, R., Kay, P., Foulger, M. (2008). The use of GIS and multi-criteria evaluation (MCE) to identify agricultural land management practices which cause surface water pollution in drinking water supply catchments. *Water Science and Technology*, **58**(9), 1797-1802.

Grottke, M. (1987). Runoff quality from a street with medium traffic loading. *The Science of the Total Environment*, **59** 457-466.

Haiping, Z., Yamada, K. (1998). Simulation of nonpoint source pollutant loadings from urban area during rainfall: an application of a physically-based distributed model. *Water Science and Technology*, **38**(10), 199-206.

Haith, D. A. (1999). *RUNQUAL - Runoff quality from development sites*. Report Users manual, Department of Agricultural & Biological Engineering, Cornell University, Ithaca, New York, USA.

Hatt, B.E., Fletcher, T. D., Deletic, A. (2009a). Hydrologic and pollutant removal performance of stormwater biofiltration systems at the field scale. *Journal of Hydrology*, **365**(3-4), 310-321.

Hatt, B.E., Fletcher, T. D., Deletic, A. (2009b). Pollutant removal performance of field-scale stormwater biofiltration systems. *Water Science and Technology*, **59**(8), 1567-1576.

He, W., Odnevall Wallinder, I., Leygraf, C. (2002). A laboratory study of copper and zinc runoff during first flush and steady-state conditions. *Corrosion Science*, **43**(1), 127-146.

- Henze, M., Gujer, W., Takashi, M., and van Loosdrecht, M. (2000). *Activated Sludge Models ASM1, ASM2, ASM2d and ASM3*. Report 9, IWA Publishing, London, UK.
- Hipp, J.A., Ogunseitan, O., Lejano, R., Smith, C. S. (2006). Optimization of Stormwater Filtration at the Urban/Watershed Interface. *Environmental Science and Technology*, **40**(15), 4794-4801.
- Huber, W. C., Cannon L., and Stouder M. (2006). *BMP modeling concepts and simulation*. Report EPA/600/R-06/033, US Environmental Protection Agency, Office of Research and Development, Washington DC, USA.
- Hvitved-Jacobsen, T., Johansen, N. B., Yousef, Y. A. (1994). Treatment systems for urban and highway run-off in Denmark. *The Science of the Total Environment*, **146-147** 499-506.
- Jakeman, A.J., Letcher, R. A., Norton, J. P. (2006). Ten iterative steps in development and evaluation of environmental models. *Environmental Modelling and Software*, **21**(5), 602-614.
- Jansons, K., German, J., Howes, T. (2005). Evaluating hydrodynamic behaviour and pollutant removal in various stormwater treatment pond configurations. In: *Proceedings of the 10th International Conference on Urban Drainage*, Copenhagen, Denmark, 21st-26th August 2005.
- Jin, X., Xu, C.-Y., Zhang, Q., Singh, V. P. (2010). Parameter and modeling uncertainty simulated by GLUE and a formal Bayesian method for a conceptual hydrological model. *Journal of Hydrology*, **383**(3-4), 147-155.
- Johnson, G.D., Myers, W. L., Patil, G. P. (2001). Predictability of surface water pollution loading in Pennsylvania using watershed-based landscape measurements. *Journal of the American Water Resources Association*, **37**(4), 821-835.
- Jørgensen, S. E., Bendoricchio, G. (2001). *Fundamentals of Ecological Modelling (3rd ed.)*. Elsevier, Amsterdam, The Netherlands.
- Jungnickel, C., Stock, F., Brandsch, T., Rancke, J. (2008). Risk assessment of biocides in roof paint. *Environmental Science and Pollution Research International*, **15**(3), 258-268.
- Kadlec, R. (2000). The inadequacy of first-order treatment wetland models. *Ecological Engineering*, **15**(1-2), 105-119.
- Kanso, A., Tassin, B., Chebbo, G. (2005). A benchmark methodology for managing uncertainties in urban runoff quality models. *Water Science and Technology*, **51**(2), 163-170.
- Kanso, A., Chebbo, G., Tassin, B. (2006). Application of MCMC-GSA model calibration method to urban runoff quality modeling. *Reliability Engineering and System Safety*, **91**(10-11), 1398-1405.
- Karlaviciene, V., Švediene, S., Marčiulioniene, D. E., Randerson, P., Rimeika, M., Hogland, W. (2009). The impact of storm water runoff on a small urban stream. *Journal of Soils and Sediments*, **9**(1), 6-12.

- Kayhanian, M., Stransky, C., Bay, S., Lau, S.-L., Stenstrom, M. K. (2008). Toxicity of urban highway runoff with respect to storm duration. *Science of the Total Environment*, **389**(2-3), 386-406.
- Kim, K., Ventura, S. J., Harris, P. M. (1993). Urban Non-point-source Pollution Assessment Using a Geographical Information System. *Journal of Environmental Management*, **39**(3), 157-170.
- Kim, L.-H., Kayhanian, M., Lau, S.-L., Stenstrom, M. K. (2005). A new modelling approach for estimating first flush metal mass loadings. *Water Science and Technology*, **51**(3-4), 159-167.
- Kim, L.-H., Zoh, K. D., Jeong, S., Kayhanian, M., Stenstrom, M. K. (2006). Estimating pollutant mass accumulation on highways during dry periods. *Journal of Environmental Engineering*, **132**(9), 958-993.
- Kleidorfer, M., Deletic, A., Fletcher, T. D., Rauch, W. (2009). Impact of input data uncertainties on urban stormwater model parameters. *Water Science and Technology*, **60**(6), 1545-1554.
- Larm, T. (2003). StormTac v.2005-03 - An operative watershed management model for estimating actual and acceptable pollutant loads on receiving waters and for the design of corresponding required treatment facilities. Report
- Le Coustumer, S., Barraud, S. (2007). Long-term hydraulic and pollution retention performance of infiltration systems. *Water Science and Technology*, **55**(4), 235-243.
- Lee, E.R., Mostaghimi, S., Wynn, T. M. (2002). A model to enhance wetland design and optimize nonpoint source pollution control. *Journal of the American Water Resources Association*, **38**(1), 17-32.
- Lindblom, E., Ahlman, S., Mikkelsen, P. S. (2007a). How uncertain is model-based prediction of copper loads in stormwater runoff? *Water Science and Technology*, **56**(6), 65-72.
- Lindblom, E., Madsen, H., Mikkelsen, P. S. (2007b). Comparative uncertainty analysis of copper loads in stormwater systems using GLUE and grey-box modeling. *Water Science and Technology*, **56**(6), 11-18.
- Lindblom, E., Ahlman, S., Mikkelsen, P.S. Uncertainty-based calibration and prediction of a stormwater surface accumulation-washout model using sampled Zn, Cu, Pb and Cd field data. Submitted manuscript.
- Lindgren, Å. (2001). *Dagvattenbelastning på sjöar och vattendrag I förhållande till andra föroreningskällor*. Report Publication 2001:114, Swedish Road Administration, Borlänge, Sweden.
- Mantovan, P., Todini, E. (2006). Hydrological forecasting uncertainty assessment: Incoherence of the GLUE methodology. *Journal of Hydrology*, **330**(1-2), 368-381.

- Matott, L.S., Babendreier, J. E., Purucker, S. T. (2009). Evaluating uncertainty in integrated environmental models: A review of concepts and tools. *Water Resources Research*, **45**(6), W06421.
- McQueen, A.D., Johnson, B. M., Rodgers, J. H. J., English, W. R. (2010). Campus parking lot stormwater runoff: Physicochemical analyses and toxicity tests using *Ceriodaphnia dubia* and *Pimephales promelas*. *Chemosphere*, **79**(5), 561-569.
- Mitchell, G. (2005). Mapping hazard from urban non-point pollution: a screening model to support sustainable urban drainage planning. *Journal of Environmental Management*, **74**(1), 1-9.
- Mitchell, V.G., Diaper, C. (2005). UVQ: A tool for assessing the water and contaminant balance impacts of urban development scenarios. *Water Science and Technology*, **52**(12), 91-98.
- Modaresi, R., Westerlund, C., Viklander, M. (2010). Estimation of pollutant loads transported by runoff by using a GIS model. Case study: Luleå city centre. In: *Proceedings of 7th Novatech 2010 - Sustainable techniques and strategies in urban water management*, Lyon, France, 27th July-1st July.
- Morris, M.D. (1991). Factorial sampling plans for preliminary computational experiments. *Technometrics*, **33**(2), 161-174.
- Mouratiadou, I., Topp, C., Moran, D., Russel, G., Louhichi, K. (2010). Modelling common agricultural policy-water framework directive interactions and cost-effectiveness of measures to reduce nitrogen pollution. *Water Science and Technology*, **61**(10), 1689-2697.
- MUSIC development team (2005). *MUSIC manual - version 3.0.1*. Report of the CRC for Catchment Hydrology, Monash University, Australia.
- Nordeidet, B., Nordeide, T., Åstebøl, S. O., Hvitved-Jacobsen, T. (2004). Prioritising and planning of urban stormwater treatment in the Alna watercourse in Oslo. *The Science of the Total Environment*, **334-335** 231-238.
- Obropta, C.C., Kardos, J. S. (2007). Review of urban stormwater quality models: Deterministic, stochastic, and hybrid approaches. *Journal of the American Water Resources Association*, **43**(6), 1508-1523.
- Odnevall Wallinder, I., Bahar, B., Leygraf, C., Tidblad, J. (2007). Modelling and mapping of copper runoff for Europe. *Journal of Environmental Monitoring*, **9**(1), 66-73.
- Odnevall Wallinder, I., Bertling, S., Zhang, X., Leygraf, C. (2004). Predictive models of copper runoff from external structures. *Journal of Environmental Monitoring*, **6**(8), 704-712.
- Opher, T., Friedler, E. (2009). A preliminary coupled MT-GA model for the prediction of highway runoff quality. *Science of the Total Environment*, **407**(15), 4490-4496.
- Osuch-Pajszinska, E., Zawilski, M. (1998). Model of storm sewer discharge. I: description. *Journal of Environmental Engineering*, **124**(7), 593-598.

- Park, M.H., Pincetl, S., Stenstrom, M. K. (2008). Water quality improvement by implementation of Proposition O in the Los Angeles river watershed, California. *Water Science and Technology*, **58**(22), 2271-2278.
- Park, M.H., Stenstrom, M. K. (2009). Classifying environmentally significant urban land uses with satellite imagery. *Journal of Environmental Management*, **86**(1), 181-192.
- Park, M.H., Swamikannu, X., Stenstrom, M. K. (2009). Accuracy and precision of the volume-concentration method for urban stormwater modeling. *Water Research*, **43**(11), 2773-2786.
- Pathapati, S.-S., Sansalone, J. (2009). CFD Modeling of a Storm-Water Hydrodynamic Separator. *Journal of Environmental Engineering*, **135**(4), 191-202.
- Persson, J., Somes, N. L. G., Wong, T. H. F. (1999). Hydraulics efficiency of constructed wetlands and ponds. *Water Science and Technology*, **40**(3), 291-300.
- Pitt, R., Lilburn, M., Durrans, S. R., Burian, S., Nix, S., Voorhees, J., and Martinson, J. (1999). Guidance Manual for Integrated Wet Weather Flow (WWF) Collection and Treatment Systems for Newly Urbanized Areas (New WWF Systems) - Final Project Report. Report. National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency. Cincinnati, Ohio, USA.
- Pitt, R., Maestre, A. (2005). Stormwater quality as described in the National Stormwater Quality Database (NSQD). In: *Proceedings of the 10th International Conference on Urban Drainage*, Copenhagen, Denmark, 21st-26th August 2005.
- Pitt, R., Voorhees, J. (2002). SLAMM, the Source Loading and Management Model. In: *Wet-Weather Flow in the Urban Watershe: Technology and Managment*, Field, R. and Sullivan, D. (eds.), CRC Press, Boca Raton, Florida, USA.
- Pujol, G. (2009). Simplex-based screening designs for estimating metamodels. *Reliability Engineering and System Safety*, **94**(7), 1156-1160.
- Qiu, Z., Prato, T. (1999). Accounting for spatial characteristics of watersheds in evaluationg water pollution abatement policies. *Journal of Agricultural and Applied Economics*, **31**(1), 161-175.
- Refsgaard, J.C., van der Sluijs, J. P., Højberg, A. L., Vanrolleghem, P. A. (2007). Uncertainty in the environmental modelling process - A framework and guidance. *Environmental Modelling and Software*, **22**(11), 1543-1556.
- Reichert, P., Borchardt, D., Henze, M., Rauch, W., Shanahan, P., Somlyódy, L., and Vanrolleghem, P. A. (2001). *River Water Quality Model No. 1*. Report Scientific and Technical Report No. 12, IWA Publishing, London, UK.
- Revitt, M., Scholes, L., Ellis, J. B. (2008). A pollutant removal prediction tool for stormwater derived diffuse pollution. *Water Science and Technology*, **57**(8), 1257-1264.

- Robien, A., Striebel, T., Herrmann, R. (1997). Modeling of dissolved and particle-bound pollutants in urban street runoff for source area watersheds. *Water Science and Technology*, **36**(8-9), 77-82.
- Rossi, L., Krejci, V., Rauch, W., Kreikenbaum, S., Fankhauser, R., Gujer, W. (2005). Stochastic modeling of total suspended solids (TSS) in urban areas during rain events. *Water Research*, **39**(17), 4188-4196.
- Rossman, L. A. (2009). *Storm Water Management Model user's manual - version 5.0*. Report EPA/600/R-05/40, U.S. Environmental Protection Agency, Cincinnati, Ohio, USA.
- Ruan, M., Wiggers, J. B. M. (1997). A conceptual CSO emission model: SEWSIM. *Water Science and Technology*, **37**(1), 259-267.
- Saltelli, A. (2000). What is sensitivity analysis. In: *Sensitivity Analysis*, Saltelli A., Chan K, and Scott E.M. (eds.), John Wiley & Sons, Chichester, UK.
- Saltelli, A., Annoni, P. (2010). How to avoid a perfunctory sensitivity analysis. *Environmental Modelling and Software*, **25**(12), 1508-1517.
- Saltelli, A., Ratto, M., Tarantola, S., Campolongo, F. (2006). Sensitivity analysis practices: Strategies for model-based inference. *Reliability Engineering and System Safety*, **91**(10-11), 1109-1125.
- Sartor, J.D., Boyd, G. B., Agardy, F. J. (1974). Water pollution aspects of street surface contaminants. *Journal Water Pollution Control Federation*, **46**(3), 458-467.
- Schellart, A.N.A., Tait, S. J., Ashley, R. M. (2010). Towards quantification of uncertainty in predicting water quality failures in integrated catchment model studies. *Water Research*, **44**(13), 3893-3904.
- Schoknecht, U., Gruycheva, J., Mathies, H., Bergmann, H., Burkhardt, M. (2009). Leaching of Biocides Used in Façade Coatings under Laboratory Test Conditions. *Environmental Science and Technology*, **43**(24), 9321-9328.
- Scholes, L., Revitt, M., Ellis, J. B. (2008a). A systematic approach for the comparative assessment of stormwater pollutant removal potentials. *Journal of Environmental Management*, **88**(3), 467-478.
- Scholes, L., Revitt, M., Lützhøft, H.-C. H., Eriksson, E. (2008b). Assessment of the removal potentials of selected EU WFD priority pollutants within stormwater Best Management Practices.
- Shafer, M.M., Hoffmann, S. R., Overdier, J. T., Armstrong, D. E. (2004). Physical and kinetic speciation of copper and zinc in three geochemically contrasting marine estuaries. *Environmental Science and Technology*, **38**(14), 3810-3819.
- Shaw, S.B., Walter, M. T., Steenhuid, T. S. (2006). A physical model of particulate wash-off from rough impervious surfaces. *Journal of Hydrology*, **327**(3-4), 618-626.

Smith, P., Beven, K. J., Tawn, J. A. (2008). Informal likelihood measures in model assessment: Theoretic development and investigation. *Advances in Water Resources*, **31**(8), 1087-1100.

Stockholm Vatten (2006) *SORBUS Reningsanläggning för dagvatten (SORBUS treatment for stormwater)* (in Swedish). Report nr. 12-2006. Stockholm Vatten AB. Stockholm, Sweden.

Trapp, S., Harland, B. (1995). Field Test of Volatilization Models. *ESPR - Environmental Science and Pollution Research - International*, **2**(3), 164-169.

Tsihrintzis, V.A., Hamid, R. (1997). Modeling and management of urban stormwater runoff quality: a review. *Water Resources Research*, **11**(2), 137-164.

Vaze, J., Chiew, F. H. S. (2002). Experimental study of pollutant accumulation on an urban road surface. *Urban Water*, **4**(4), 379-389.

Vaze, J., Chiew, F. H. S. (2003a). Comparative evaluation of urban storm water quality models. *Water Resources Research*, **39**(10), SWC51-SWC510.

Vaze, J., Chiew, F. H. S. (2003b). Study of pollutant washoff from small impervious experimental plots. *Water Resources Research*, **39**(6), HWC31-HWC310.

Vollertsen, J., Asbjørn Haaning, N., Hvitved-Jacobsen, T., Åstebøl, S. O., Coward, J. E., Fageraas, T. (2009). Performance and modelling of a highway wet detention pond designed for cold climate. *Water Quality Research Journal of Canada*, **44**(3), 253-262.

Vollertsen, J., Åstebøl, S. O., Coward, J. E., Fageraas, T., Madsen, H. I., Nielsen, A. H., Hvitved-Jacobsen, T. (2007). Monitoring and modelling the performance of a wet pond for treatment of highway runoff in cold climates. In: *Proceedings of the 8th Highway and Urban Environment*. Springer, Dordrecht, The Netherlands.

Vrugt, J.A., Gupta, H. V., Bouten, W., Sorooshian, S. (2003). A Shuffled Complex Evolution Metropolis algorithm for optimization and uncertainty assessment of hydrologic model parameters. *Water Resources Research*, **38**(8), SWC11-SWC116.

Walker, D.J., Hurl, S. (2002). The reduction of heavy metals in a stormwater wetland. *Ecological Engineering*, **18**(4), 407-414.

Walker, W.E., Harremoës, P., Rotmans, J., van der Sluijs, J. P., van Asselt, M. B. A., Janssen, P., Kreyer von Krauss, M. P. (2003). Defining Uncertainty: A Conceptual Basis for Uncertainty Management in Model-Based Decision Support. *Integrated Assessment*, **4**(1), 5-17.

Walker, W. W. (1990). *P8 Urban Catchment Model - Program Documentation version 1.1*. Report prepared for IEP, Inc and Narragansett Bay Project, Concord, Massachusetts, USA.

Walker, W.W., Kadlec, R. (2008). Dynamic Model for Stormwater Treatment Areas - Model Version 2. Homepage prepared for the *U.S. Department of the Interior & U.S. Army Corps of Engineers* (www.walker.net/dmsta/index.htm).

- Warmink, J.J., Janssen, J. A. E. B., Booij, M. J., Krol, M. S. (2010). Identification and classification of uncertainties in the application of environmental models. *Environmental Modelling and Software*, **25**(12), 1518-1527.
- Wayne County (1998). *User's Manual: Watershed Management Model version 4.1*. Report Rouge River National Wet Weather Demonstration Project, Technical Memorandum RPO-NPS-TM27.02, Wayne County, Michigan, USA.
- Werner, T.M., Kadlec, R. H. (2000). Wetland residence time distribution modeling. *Ecological Engineering*, **15**(1-2), 77-90.
- Willems, P. (2008). Quantification and relative comparison of different types of uncertainties in sewer water quality modeling. *Water Research*, **42**(13), 3539-3551.
- Wright Water Engineers (2007). *International Stormwater BMP Database*. Developed by Wright Water Engineers, Inc. and Geosyntec Consultants for the Water Environment Research Foundation (WERF), the American Society of Civil Engineers (ASCE)/Environmental and Water Resources Institute (EWRI), the American Public Works Association (APWA), the Federal Highway Administration (FHWA), and U.S. Environmental Protection Agency (EPA).
- Wong, T.H.F., Fletcher, T. D., Duncan, H. P., Jenkins, G. A. (2006). Modelling urban stormwater treatment - A unified approach. *Ecological Engineering*, **27**(1), 58-70.
- Yang, Y.S., Wang, L. (2010). A Review of Modelling Tools for Implementation of the EU Water Framework Directive in Handling Diffuse Water Pollution. *Water Resources Management*, **24**(9), 1819-1843.
- Yu, S. L., Fitch, G. M., Earles, T. A. (1998). *Constructed Wetlands for Stormwater Management - Final Report*. Report VTRC 98-R35, Virginia Transportation Research Council, Charlottesville, Virginia, USA.
- Yuan, Y., Hall, K., Oldham, C. (2001). A preliminary model for predicting heavy metal contaminant loading from an urban catchment. *The Science of the Total Environment*, **266**(1-3), 299-307.
- Zheng, J., Shoemaker, L., Riverson, J., Khalid, A., Cheng, M.-S. (2006). BMP analysis system for watershed-based stormwater management. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, **41**(7), 1391-1403.
- Zug, M., Bellefleur, D., Phan, L., Scrivener, O. (1999a). HORUS: a conceptual model of pollution simulation in sewer networks. *Water Science and Technology*, **39**(9), 31-38.
- Zug, M., Phan, L., Bellefleur, D., Scrivenes, O. (1999b). Pollution wash-off modelling on impervious surfaces: calibration, validation, transposition. *Water Science and Technology*, **39**(2), 17-24.

Appendices

- I.** **Vezzaro, L.**, Mikkelsen, P.S.; Application of global sensitivity analysis and uncertainty quantification in dynamic modelling of micropollutants in stormwater runoff. Submitted manuscript.
- II.** **Vezzaro, L.**, Eriksson, E., Ledin, A., Mikkelsen, P.S. (2010); Dynamic stormwater treatment unit model for micropollutants (STUMP) based on substance inherent properties. *Water Science and Technology*; **62**(3), 622-629.
- III.** **Vezzaro, L.**, Eriksson, E., Ledin, A., Mikkelsen, P.S.; Modelling the fate of organic micropollutants in stormwater ponds. Submitted manuscript.
- IV.** **Vezzaro, L.**, Eriksson, E., Ledin, A., Mikkelsen, P.S.; Quantification of uncertainty in modelled partitioning and removal of heavy metals (Cu, Zn) in a stormwater retention pond and a biofilter; Submitted manuscript.
- V.** **Vezzaro, L.**, Ledin, A., Mikkelsen, P.S. (2010). Integrated modelling of priority pollutants in stormwater systems. In *Proceedings of IDRA 2010. XXXII Italian Conference of Hydraulics and Hydraulic Constructions*, Palermo, Italy, 14th-17th September 2010.
- VI.** Estimation of Copper fluxes in the Basin K catchment, Albertslund, Denmark. Manuscript.
- VII.** Use of the SCEM-UA sampler in uncertainty analysis. Manuscript.

The papers above are not included in this www-version but can be obtained from the library at DTU Environment. Contact info: Library, Department of Environmental Engineering, Technical University of Denmark, Miljoevej, Building 113, DK-2800 Kgs. Lyngby, Denmark or library@env.dtu.dk.

The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four themes:
Water Resource Engineering, Urban Water Engineering,
Residual Resource Engineering and Environmental Chemistry & Microbiology.
Each theme hosts two to five research groups.

The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

DTU Environment
Department of Environmental Engineering
Technical University of Denmark

Miljoevej, building 113
DK-2800 Kgs. Lyngby
Denmark

Phone: +45 4525 1600
Fax: +45 4593 2850
e-mail: reception@env.dtu.dk
www.env.dtu.dk

ISBN 978-87-92654-26-7